Supporting Information

Site-Selective Copper-Catalyzed Azidation of Benzylic C–H Bonds

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1. General Information

Materials and spectroscopic methods. Cu salts were purchased from Sigma Aldrich. Benzylic C–H substrates and the reagents for the syntheses were purchased from Oakwood Chemicals, Combi-Blocks, Chem-Impex, Alfa Aesar, TCI America, Ark Pharm, Enamine, AstaTech or Sigma Aldrich, and were used without further purification. TMS-N_3 was purchased from Sigma Aldrich. Ligands were purchased from Aldrich or TCI America. *N*-Fluorobenzenesulfonimide (NFSI) was purchased from Ark Pharm. The solvents were purchased from Fisher Scientific or Sigma Aldrich. The silica gel (particle size 40-63 μm, 230-400 mesh) that was used for flash column chromatography and thin layer chromatography plates (250 μm thickness) were purchased from SiliCycle. The photoreactions were carried out with two Par38 LED lamps supplying blue light (λ = 440-460 nm). The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on either a Bruker 400 MHz spectrometer or a Bruker 500 MHz spectrometer. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus by the mass spectrometry facility at the University of Wisconsin-Madison. IR spectra were recorded on a Bruker Platinum-ATR ALPHA spectrometer. Melting points were determined using a DigiMelt MPA160 SRS melting point apparatus. Optical rotation was obtained using a Rudolph Research Autopol III polarimeter at room temperature. Elemental analysis was performed by Midwest Microlab, LLC. Enantioselectivities were determined by SFC/MS analyses on a Waters TharInvestigator equipped with a Daicel CHIRALCEL® OD-H HPLC analytical column (particle size 5 μm, ID 4.6 mm x L 250 mm).

Safety Consideration for Organic Azides[1,2]

Azides are potentially explosive chemicals (PECs) that can decompose under the impact from external sources (heat, light, pressure, and shock). They should be stored in locations away from light, pressure, and shock at below room temperature. A blast shield should be placed around the reaction vessels containing the azides. The total number of nitrogen atoms in organic azide compounds should not surpass that of carbon. Azide compounds with a ratio of $(N_{Carbon} + N_{Oxygen}) / N_{Nitrogen} \geq 3$ are generally stable. Azide compounds with $(N_{Carbon} + N_{Oxygen}) / N_{Nitrogen}$ ratio between 1 and 3 can be synthesized and isolated but should be stored below room temperature with $\leq$1 M concentration and at a maximum of 5 grams of material. Isolation of azides with $(N_{Carbon} + N_{Oxygen}) / N_{Nitrogen}$ ratio < 1 are not allowed. Azide and acidic wastes should not be mingled as highly toxic and explosive hydrazoic acid can be generated. Azide waste should be stored in a container designated only for azide waste.

Computational Methods

For all computed structures, density functional theory (DFT) calculations are performed with the Gaussian 16 (rev. C.01) electronic structure program suite.[3] Geometries of all stationary points are optimized in the *gas phase* at the B3LYP-D3(BJ)/basis-I level of theory,[4,5] where *basis-I* comprises the 6-31G(d,p) basis[6] for non-metals and the Stuttgart/Dresden effective core potential with its associated basis set (SDD) for Cu.[7] For numerical integration in DFT, "ultrafine" grid is chosen together with the default integral accuracy set at 10^{-12}. Vibrational frequency calculations were performed at the same level of theory to ensure natures of all stationary points. Frequencies below 50 cm^{-1} were replaced by a value of 50 cm^{-1} in the vibrational partition function when computing thermal contributions to free energies (1 atm pressure, T = 298.15K). For better estimate to Gibbs free energies, single point electronic energies were recomputed using M06-L/basis-II level of theory[8] where *basis-II* consists of the def2-TZVP basis[9] for non-metals and def2-TZVP basis/SDD pseudo potential for Cu. Solvation effects were included employing the SMD continuum solvation model[10] with solvent parameters for nitromethane (ε = 36.562).

For the series of reactions (Figure S10; Path-II) of the doublet benzylic radical with the triplet $[LCu^{II}(N_3)_2]_2$ dimer, yielding a benzylic azide product and the $LCu^{I}(N_3)$ species, both having closed shell singlet

electronic structures, along with the doublet [$LCu^{II}(N_3)_2$] monomer species, the corresponding transition-state (TS) structures were located on the broken-symmetry (BS) surface. In those cases, the spin-projection scheme of Yamaguchi et al.[11] was used for obtaining approximate spin-projected electronic energies of the lower-spin states using equation (S1). Redox potentials of various species were also computed (at 298.15 K) using the above-mentioned protocol. For the redox transformation: O(sol) + ne^-(g) $\rightarrow$ R(sol), standard reduction potential has been computed using equation (S2).

$$E_{AP}^{LS} = E^{HS} + \left(E_{BS}^{LS} - E^{HS}\right) \times \frac{\langle \hat{S}^2 \rangle_{exact}^{HS} - \langle \hat{S}^2 \rangle_{exact}^{LS}}{\langle \hat{S}^2 \rangle^{HS} - \langle \hat{S}^2 \rangle_{BS}^{LS}} \quad \text{(S1)}$$

Where, E = electronic energy, BS = broken (spin) symmetry, AP = approximate (spin) projection, LS = low-spin, HS = high-spin.

$$E_{O|R}^{0} = \frac{G^0(O,sol) - G^0(R,sol)}{n_e F} - E_{reference}^{0} \quad \text{(S2)}$$

Where, n_e = 1, F is the Faraday constant. We first report *absolute* reduction potentials of various species setting $E_{reference}^{0}$ at 0 V. Corresponding values vs. the $Fc^{0/+}$ reference were then calculated using an empirical correction factor accounting for experimentally available redox data, as detailed in Section S9 (Computed Reduction Potentials).

Cartesian Coordinates of Structures

Cartesian coordinates of all DFT-optimized structures can be accessed from the coordinate file (.xyz).

2. General Procedure for Cu-Catalyzed Benzylic C-H Azidation

Procedure A: A 4 mL borosilicate glass vial was charged with benzylic substrate (0.4 mmol), 2.0 mol% of copper(II) acetate (1.5 mg, 8.0 μmol), 4.0 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (5.1 mg, 16 μmol), 2.5 equivalents of *N*-fluorobenzenesulfonimide (315 mg, 1.00 mmol), and a magnetic stir bar outside a glovebox. The vial was capped with an open-top cap installed with a TFE lined silicone SURE-LINK™ septum. The septum cap was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the vial was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the vial was removed from the glovebox. The vial was charged with nitromethane (2.0 mL, 0.20 M) and 3.6 equivalents of azidotrimethylsilane (190 μL, 1.44 mmol) sequentially, stirred, and heated to 30 ℃ (inner temperature) in a heating block on a hot plate. After 24 hours, the vial was cooled to room temperature (25 ℃), charged with 3.0 equivalents of Li_2CO_3 (89 mg, 1.2 mmol), opened to air, and stirred for 30 minutes. The reaction mixture was then filtered through a pipette-silica plug with dichloromethane (1.0 mL x 3 times). After evaporation of solvent on a rotary evaporator at 30 ℃, flash column chromatography was performed. The isolated compound was dried to give the desired azido product.

Procedure B: Adopting Procedure A, the reaction was performed at 50 ℃ for 16 hours.

Procedure C: Adopting Procedure A, the reaction was performed for 48 hours.

Procedure D: Adopting Procedure A, the reaction was conducted in 0.2 mmol scale based on benzylic substrate. Deviation from Procedure A was 6.0 mol% of copper(II) acetate (2.2 mg, 12 μmol), 12 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (7.7 mg, 24 μmol), 2.5 equivalents of *N*-fluorobenzenesulfonimide (158 mg, 0.5 mmol), nitromethane (1.0 mL, 0.20 M), and 3.6 equivalents of azidotrimethylsilane (96 μL, 0.72 mmol). 3.0 equivalents of Li_2CO_3 (44 mg, 0.60 mmol) was used for workup process.

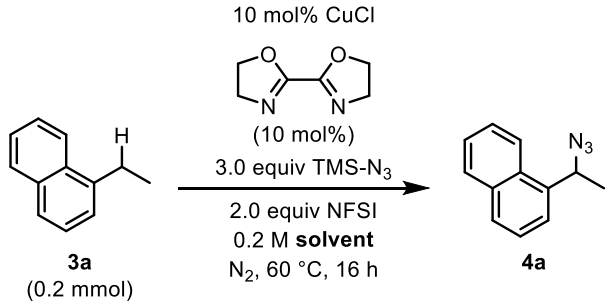
Procedure E: Adopting Procedure A, the reaction was conducted in 0.2 mmol scale based on benzylic substrate. Deviation from Procedure A was 1.0 mol% of copper(II) acetate (0.40 mg, 2.0 μmol), 2.0 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (1.3 mg, 4.0 μmol), 2.5 equivalents of *N*-fluorobenzenesulfonimide (158 mg, 0.5 mmol), nitromethane (1.0 mL, 0.20 M), and 3.6 equivalents of azidotrimethylsilane (96 μL, 0.72 mmol). 3.0 equivalents of Li_2CO_3 (44 mg, 0.60 mmol) was used for workup process.

Notes:
(1) For safety, all reaction should be performed with the use of blast shield.
(2) Calibration of hot plate is highly recommended to maintain inner reaction temperature because performance of this reaction is sensitive to temperature (especially for reactions conducted at 30 ℃; Procedure A and B).
(3) Liquid benzylic C–H substrates were added between addition of nitromethane and azidomethylsilane.
(4) Both dichloromethane (1.0 mL x 3 times) and nitromethane (1.0 mL x 3 times) were used for filtration with a pipette-silica plug.
(5) Evaporation of solvent from compound **4a** or **4b** on the rotary evaporator should be carefully conducted at low temperature due to their high volatility.
(6) Li_2CO_3 was not used for the crude mixture of compound **4t** to minimize keto-enol tautomerization.

3. Screening Tables for Reaction Optimization

Note: Reaction conditions for screening were adopted from General Procedure A.

Table S1. Optimization of the Reation Conditions with Various Solvents[a]

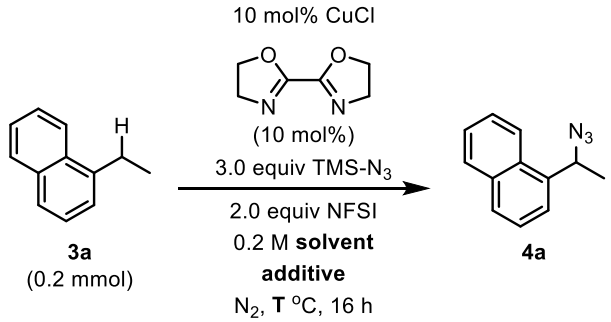


entry	solvent	conv. of **3a** (%)	yield of **4a** (%)
1	**$MeNO_2$**	**100**	**57**
2	DCE	18	7.0
3	ACN	100	49
4	PhCl	94	39
5	$PhCF_3$	9.0	-
6	$PhNO_2$	100	51
7	PhH	74	37
8	Ph_2O	11	-
9	DME	39	32
10	1,4-Dioxane	8.0	22
11	THF	21	12
12	$CHCl_3$	86	47
13	Acetone	57	32
14	EtOAc	37	20
15	DMF	30	12
16	DMAc	23	8.0

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard. DCE, 1,2-dichloroethane; ACN, acetonitrile; DME, 1,2-dimethoxyethane; THF, tetrahydrofuran; EtOAc, ethyl acetate; DMF, *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethylacetamide.

To summarize the results above. the reaction in nitromethane proceeds in the highest yield, but other polar solvents including acetonitrile, nitrobenzene, and acetone also led to a high conversion. Exceptions include the polar aprotic solvents *N*,*N*-dimethylformamide and *N*,*N*-dimethylformamide. Etherial solvents such as 1,2-dimethoxyethane, tetrahydrofuran, 1,4-dioxane, and diphenyl ether afforded poor to no yield with low conversion.

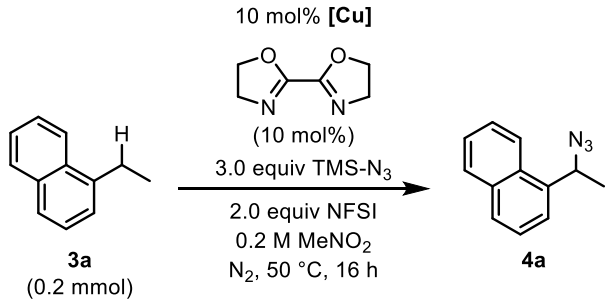
Table S2. Optimization of Reaction Conditions with Various Temperatures and Additives[a]



entry	solvent	additive	temp (**T**)	conv. of **3a** (%)	yield of **4a** (%)
1	$MeNO_2$	-	24	3.0	-
2	$MeNO_2$	-	40	37	29
3	**$MeNO_2$**	**-**	**50**	**88**	**63**
4	$MeNO_2$	-	60	100	54
5	$MeNO_2$:HFIP (4:1)	-	50	86	65
6	$MeNO_2$:HFIP (4:1)	50 mol% $(^iPrO)_2P(O)H$	50	77	37
7	$MeNO_2$	50 mol% $(^iPrO)_2P(O)H$	50	64	51
8	$MeNO_2$:HFIP (4:1)	-	24	9.0	3.0
9	$MeNO_2$:HFIP (4:1)	50 mol% $(^iPrO)_2P(O)H$	24	3.0	3.0
10	$MeNO_2$	50 mol% $(^iPrO)_2P(O)H$	24	7.0	-

[a]Reaction yields monitored by ^1H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

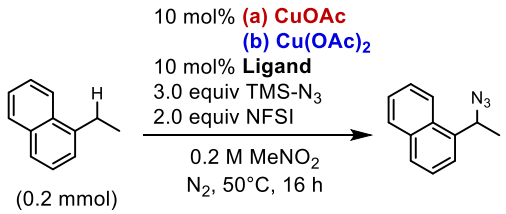
Table S3. Optimization of Reaction Conditions with Various Copper Salts[a]

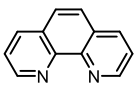
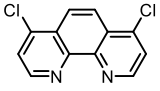
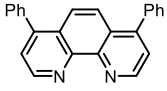
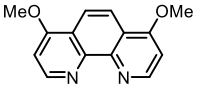
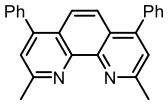
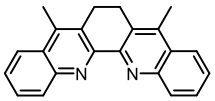
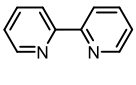
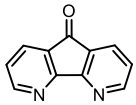
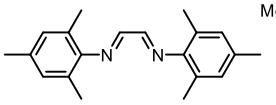
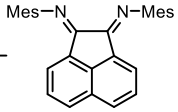
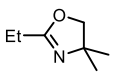
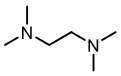
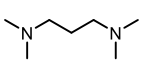
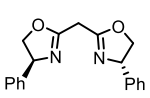
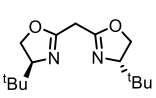
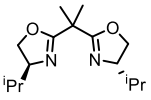
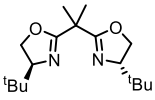
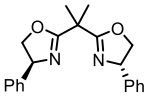
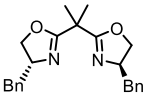
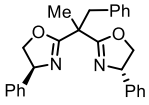
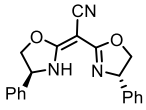
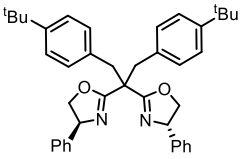
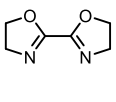
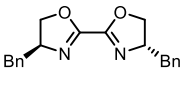
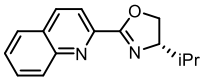
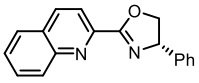
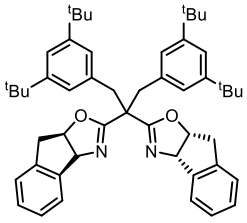
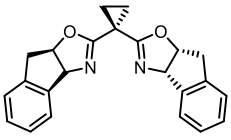
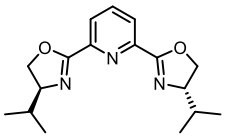
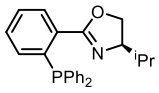
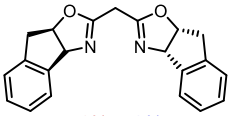
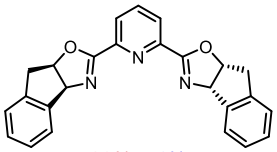
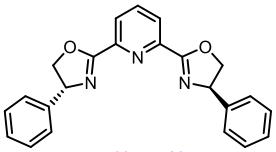


entry	[Cu]	conv. of **3a** (%)	yield of **4a** (%)
1	CuCl	90	63
2	CuBr	82	60
3	CuI	70	48
4	**CuOAc**	**89**	**69**
5	$Cu(ACN)_4PF_6$	83	39
6	$CuBr{\cdot}SMe_2$	58	29
7	Cu_2O	1.0	-
8	$CuCl_2$	88	63
9	**$Cu(OAc)_2$**	**88**	**69**
10	$Cu(acac)_2$	71	55
11	$Cu(OTf)_2{\cdot}PhH$	84	66
12	$Cu(OTf)_2{\cdot}PhMe$	64	51
13	$Cu(NO_3)_2{\cdot}2.5H_2O$	56	42
14	$CuSO_4$	72	57
15	CuPc	17	9.0
16	(*i*-Pr)CuCl	91	67

[a]Reaction yields monitored by ^1H NMR spectroscopy with 0.2 mmol mesitylene as the external standard. acac, acetylacetonate; Pc, phthalocyanine

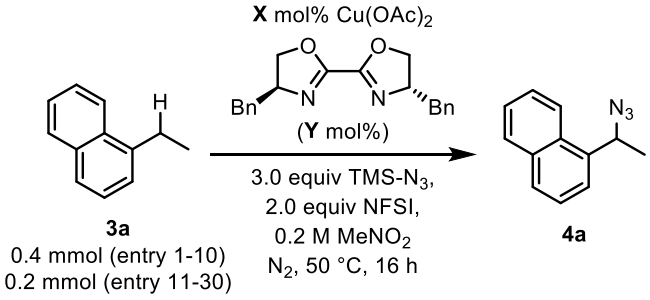
Table S4. Optimization of Reaction Conditions with Various Ligands and Copper Salts[a]



 52%	 53%	 52%	 33%	 64%	 68%
 34%	 53%	 64%	 46%	 62%	 66%	 53%	 57%
 74%, 79%	 71%, 73%	 65%, 69%	 72%, 82%	 59%, 67%	 62%, 70%	 60%, 73%
 73%, 72%	 48%, 58%	 69%, 69%	 84%, 84%	 81%, 79%	 67%, 68%
 66%, 69%	 70%, 79%	 66%, 62%	 66%, 62%		
 71%, 78%	 83%, 71%	 64%, 60%			

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

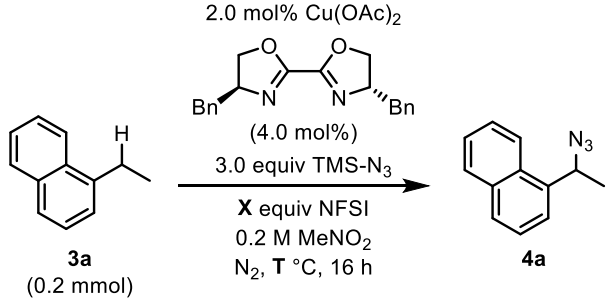
Table S5. Optimization of Reaction Conditions with Various Amounts of Copper Salts/Ligands[a]



entry	$Cu(OAc)_2$ [**X**]	ligand [**Y**]	conv. of **3a** (%)	yield of **4a** (%)
1	1.0	0.5	78	68
2	1.0	1.0	71	64
3	1.0	1.5	95	85
4	1.0	2.0	93	82
5	1.0	3.0	73	63
6	2.0	1.0	87	77
7	2.0	2.0	96	83
8	2.0	3.0	100	88
9	**2.0**	**4.0**	**100**	**89**
10	2.0	6.0	98	86
11	5.0	2.5	97	83
12	5.0	5.0	100	85
13	5.0	7.5	100	87
14	5.0	10	100	81
15	5.0	15	100	76
16	10	5.0	98	75
17	10	10	100	84
18	10	15	100	86
19	10	20	100	74
20	10	30	100	74
21	15	7.5	99	79
22	15	15	100	79
23	15	24	100	75
24	15	30	99	74
25	15	45	98	74
26	20	10	99	79
27	20	20	100	79
28	20	30	100	77
29	20	40	100	75
30	20	60	100	74

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard

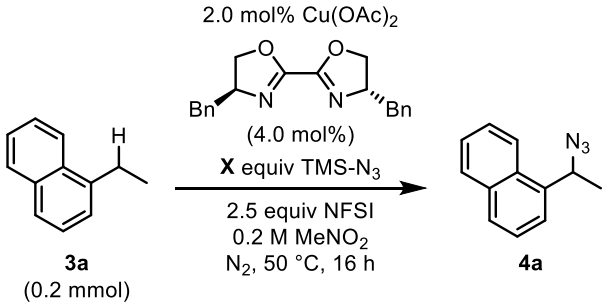
Table S6. Optimization of Reaction Conditions with Various Equivalents of NFSI/Temperature Screen[a]



entry	NFSI [**X**]	temp [**T**]	conv. of **3a** (%)	yield of **4a** (%)
1	-	30	-	-
2	0.5	30	26	24
3	1.0	30	39	32
4	1.5	30	47	36
5	2.0	30	53	40
6	2.5	30	58	42
7	3.0	30	59	50
8	4.0	30	70	51
9	-	40	-	-
10	0.5	40	40	37
11	1.0	40	65	56
12	1.5	40	76	64
13	2.0	40	82	70
14	2.5	40	92	74
15	3.0	40	95	74
16	4.0	40	97	76
17	-	50	-	-
18	0.5	50	42	40
19	1.0	50	72	70
20	1.5	50	98	87
21	2.0	50	100	89
22	**2.5**	**50**	**100**	**91**
23	3.0	50	100	86
24	4.0	50	100	86

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

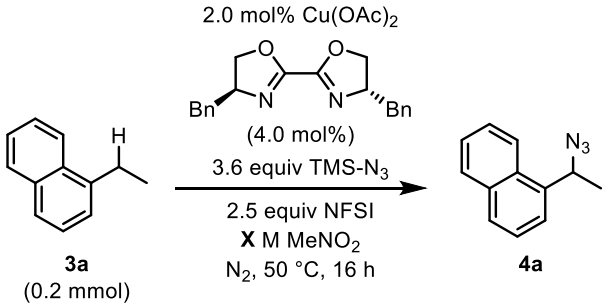
Table S7. Optimization of Reaction Conditions with Various Equivalents of TMS-N_3 Screen[a]



entry	TMS-N_3 [**X**]	conv. of **3a** (%)	yield of **4a** (%)
1	1.0	93	47
2	1.2	97	55
3	1.4	99	58
4	1.6	100	63
5	1.8	100	67
6	2.0	100	69
7	2.2	100	75
8	2.4	100	81
9	2.6	100	83
10	2.8	100	85
11	3.0	100	91
12	3.2	100	92
13	3.4	100	92
14	**3.6**	**100**	**93**
15	3.8	100	88
16	4.0	100	89
17	5.0	100	89
18	6.0	100	86
19	8.0	100	86

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

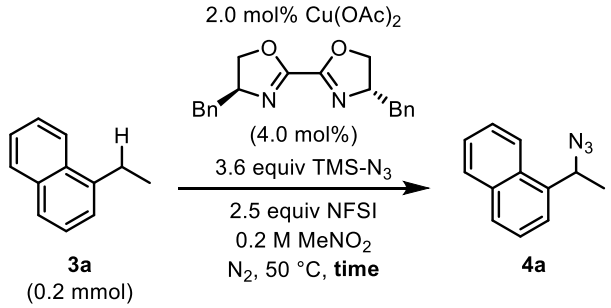
Table S8. Optimization of Reaction Conditions with Various Concentration[a]



entry	$MeNO_2$ [**X**]	conv. of **3a** (%)	yield of **4a** (%)
1	2.00	100	82
2	1.00	100	83
3	0.50	100	86
4	0.40	100	87
5	0.30	100	90
6	0.25	100	91
7	0.22	100	92
8	**0.20**	**100**	**93**
9	0.18	100	91
10	0.15	100	85
11	0.13	100	86

[a]Reaction yields monitored by ^1H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

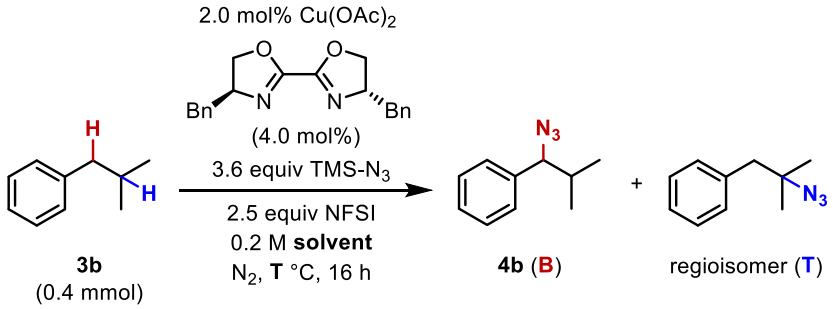
Table S9. Optimization of Reaction Conditions with Various Reaction Time[a]



entry	time	conv. of **3a** (%)	yield of **4a** (%)
1	0.5 min	-	-
2	1.0 min	-	-
3	2.5 min	1.0	1.0
4	5.0 min	3.0	3.0
5	10 min	8.0	7.0
6	15 min	12	9.0
7	20 min	12	12
8	30 min	18	17
9	40 min	21	20
10	50 min	25	24
11	1.0 h	32	31
12	1.5 h	54	40
13	2.0 h	56	47
14	2.5 h	61	52
15	3.0 h	69	59
16	4.0 h	78	67
17	5.0 h	84	75
18	6.0 h	86	80
19	8.0 h	99	89
20	12 h	100	91
21	**16 h**	**100**	**93**
22	24 h	100	90
23	32 h	100	89
24	48 h	100	85
25	72 h	100	80

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard

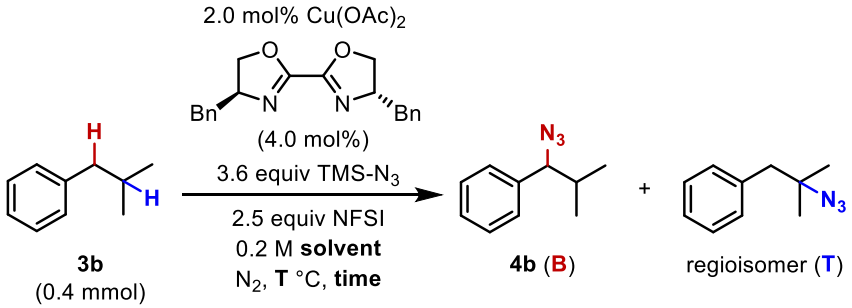
Table S10. Optimization of Benzylic C–H Site-Selectivity with Various Solvents and Temperatures[a]



entry	solvent	temp [**T**]	conv. of **3b** (%)	product (B+T) (%)	ratio (B : T)
1	$MeNO_2$	25	3	3	Only B
2	**$MeNO_2$**	**30**	**50**	**40**	**12 : 1.0**
3	$MeNO_2$	40	90	50	6.0 : 1.0
4	$MeNO_2$	50	97	46	4.6 : 1.0
5	C_6H_6	25	8	7.9	9.5 : 1.0
6	C_6H_6	30	45	32	8.8 : 1.0
7	C_6H_6	40	70	38	7.8 : 1.0
8	C_6H_6	50	85	33	5.1 : 1.0
9	PhCl	25	28	23	8.7 : 1.0
10	PhCl	30	57	37	11 : 1.0
11	PhCl	40	83	36	6.0 : 1.0
12	PhCl	50	93	26	3.4 : 1.0

[a]Reaction yields monitored by ^1H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

Table S11. Optimization of Benzylic C–H Site-Selectivity with Various Length of Reaction Time[a]



entry	solvent	temp [**T**]	time (h)	conv. of **3b** (%)	product (**B**+**T**) (%)	ratio (**B** : **T**)
1	PhCl	25	16	28	23	8.7 : 1.0
2	PhCl	25	24	45	31	12 : 1.0
3	PhCl	25	40	69	40	10 : 1.0
4	PhCl	25	64	85	34	7.1 : 1.0
5	PhCl	25	88	89	32	6.6 : 1.0
6	PhCl	25	112	91	28	7.2 : 1.0
7	PhCl	30	16	57	37	11 : 1.0
8	PhCl	30	24	75	40	9.2 : 1.0
9	PhCl	30	40	85	36	7.8 : 1.0
10	PhCl	30	64	85	29	6.9 : 1.0
11	PhCl	30	88	93	25	4.6 : 1.0
12	PhCl	30	112	96	21	3.8 : 1.0
13	C_6H_6	30	16	45	32	8.8 : 1.0
14	C_6H_6	30	24	59	38	7.5 : 1.0
15	C_6H_6	30	40	73	39	8.0 : 1.0
16	C_6H_6	30	64	84	36	4.8 : 1.0
17	C_6H_6	30	88	87	31	7.0 : 1.0
18	C_6H_6	30	112	89	29	5.4 : 1.0
19	$MeNO_2$	30	16	50	40	12 : 1.0
20	**$MeNO_2$**	**30**	**24**	**60**	**48**	**11 : 1.0**
21	$MeNO_2$	30	40	80	51	9.7 : 1.0
22	$MeNO_2$	30	64	91	56	8.1 : 1.0
23	$MeNO_2$	30	88	95	51	7.5 : 1.0
24	$MeNO_2$	30	112	97	48	7.2 : 1.0

[a]Reaction yields monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard.

4. Racemization Experiments

Yields, conversion, and enantioselectivities of azide products were determined by ^{1}H NMR spectroscopy and supercritical fluid chromatography (SFC) analysis respectively. SFC/MS analyses were performed on a Waters TharInvestigator equipped with a Daicel CHIRALCEL® OD-H HPLC analytical column (particle size 5 µm, ID 4.6 mm x L 250 mm) was used for separations of enantiomers. The sample was eluted with MeOH 20% with CO_2 at a flow rate of 3 mL/min at 35 °C with an automated backpressure regulator at 100 bar. Injection volume for each sample was 5.0 µL of a 10-30 µM solution in acetonitrile and the detection wavelength was 273 nm.

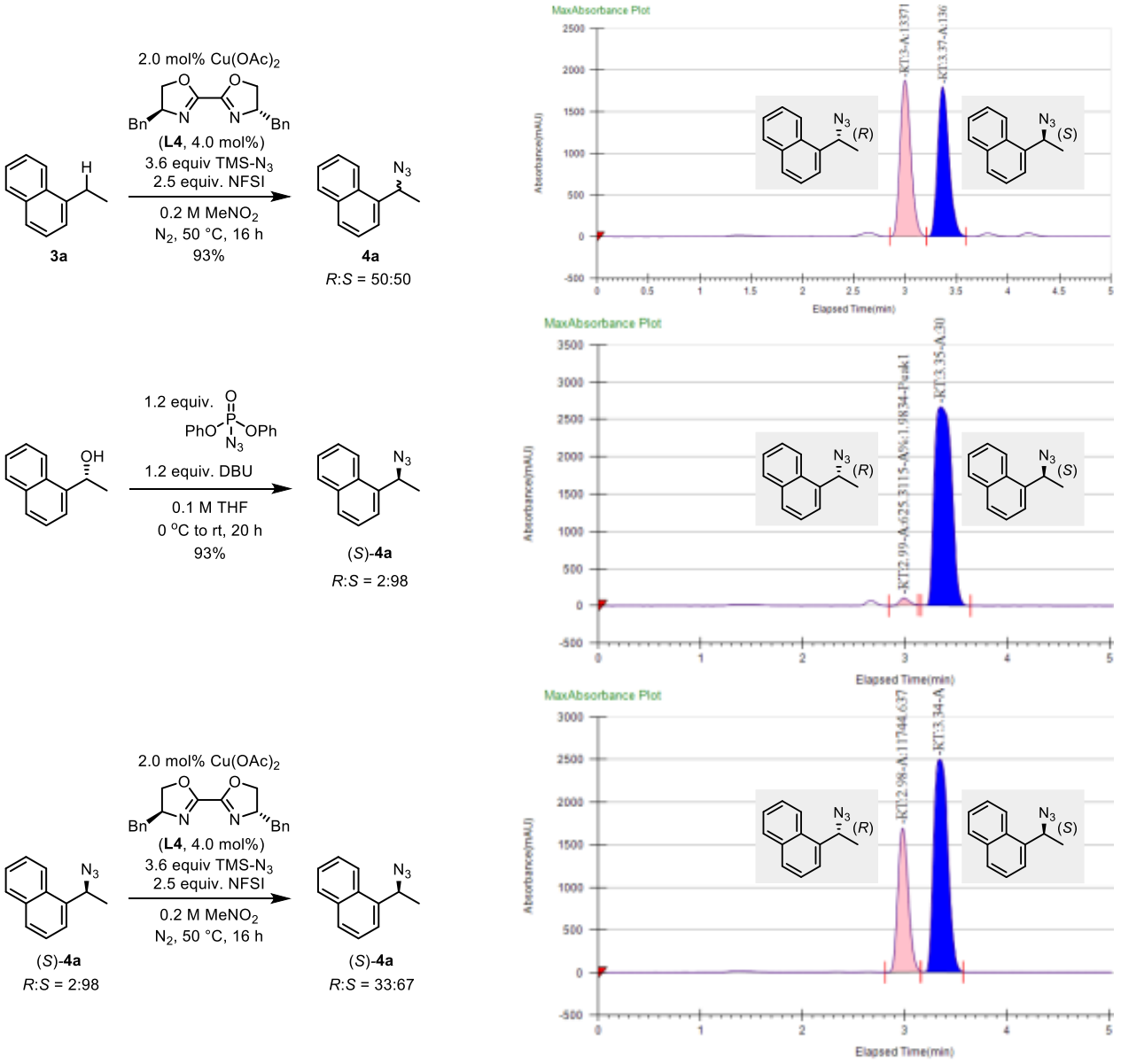


Figure S1. Supercritical fluid chromatography data.

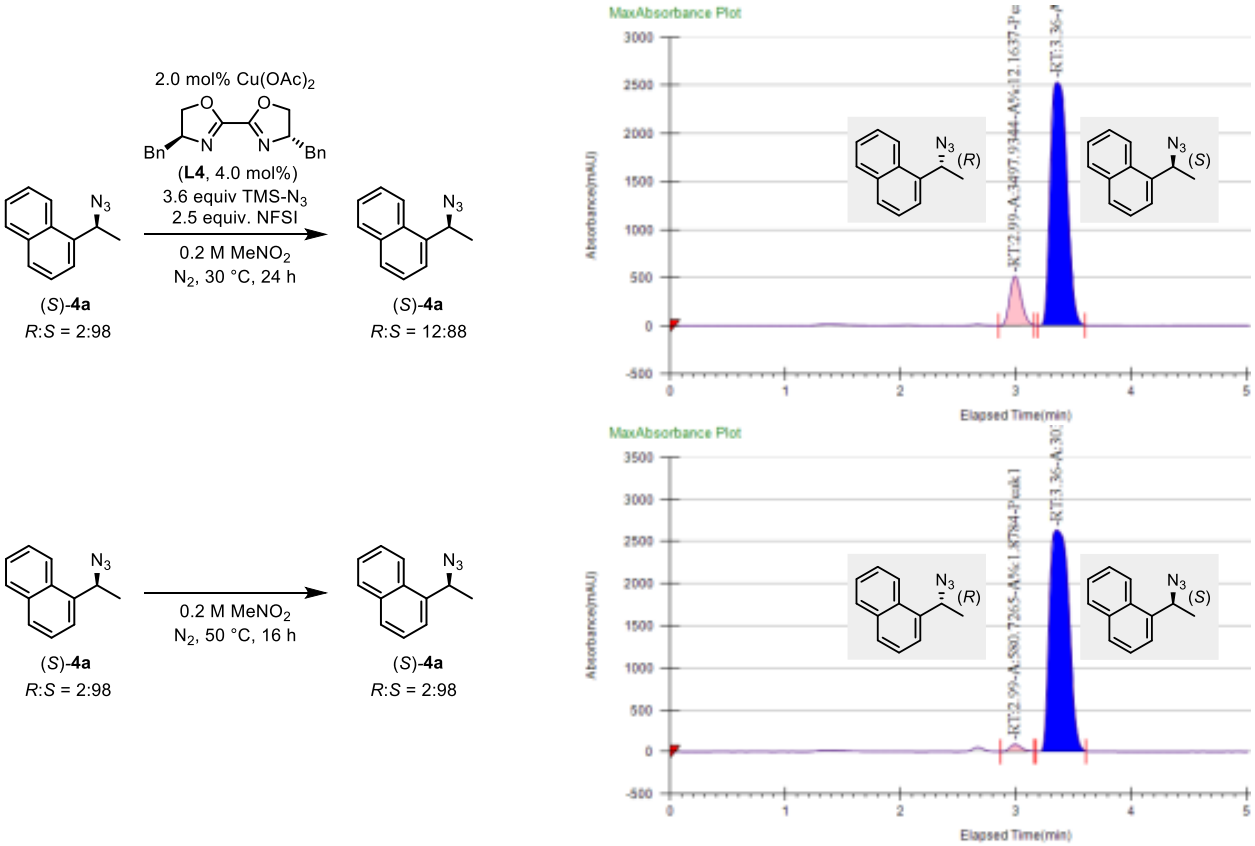
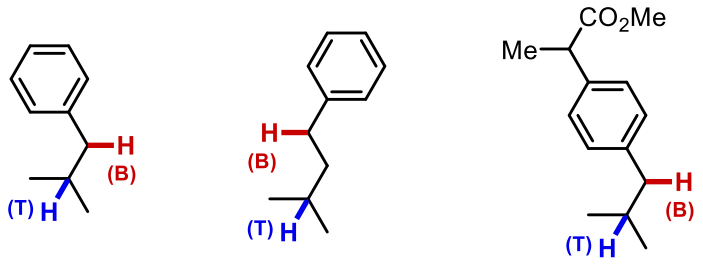


Figure S1. (Continued) Supercritical fluid chromatography data.

5. Comparative Experiments and Results with Known C-H Azidation Methods

Table S12. Tabulated Summary of Yield of Benzylic and Tertiary Azido Products[a]



3b **3c** **3d**

catalyst	Benzylic	Tertiary	Benzylic	Tertiary	Benzylic	Tertiary
Mes-Acr[b]	17.4[e]	22.6[e]	none	34.0	27.0[e]	30.0[e]
Mn(salen)Cl[c]	19.5	4.2	23.4	5.1	43.0	3.3
Fe(OAc)2·PyBOX[d]	19.4	20.6	27.8	19.9	18.0	7.0
This work	**44.0**	**4.0**	**68.0**	**2.7**	**60.0**	**2.0**

[a]Reaction yields were monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the external standard. [b]Method II. [c]Method III. [d]Method IV. [e]Yields and ratios were obtained from the literature.[12]

Method II: General Procedure for Mes-Acr System. According to the literature,[12] a 4 mL borosilicate glass vial was charged with a magnetic stir bar, 5.0 mol% of 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr, 2.9 mg, 5.0 μmol), 1.1 equivalents of K_3PO_4 (23.3 mg, 0.11 mmol), 3.0 equivalents of 4-(trifluoromethyl)benzenesulfonyl azide **S7** (75.4 mg, 0.3 mmol), hexafluoroisopropanol (HFIP, 1.0 mL), 0.1 mmol of substrate **3b** or **3c** sequentially in a glovebox. The vial was taken out of the glovebox and positioned on a stir plate with a gap of 2 cm between two Par38 LED lamps (blue light, λ = 440-460 nm). After stirring with irradiation for 20 hours, the crude solution was filtered through a pipette-silica plug with dichloromethane (1.0 mL x 3 times). Ratios of benzylic (**4b** or **4c**)[13,14] and tertiary product[15,16] were determined by ^{1}H NMR analysis of crude mixture with 0.2 mmol mesitylene as an external standard.

Note: (1) The azidation reagent (**S7**) was synthesized according to literature procedure.[17] (2) The yield and ratio of benzylic:tertiary products from **3c** was not reported by using the MES-Acr system in the literature.[12] (3) **3b** was used as a literature substrate to reproduce the reported yield (40%, isolated yield) and the ratio of regioisomers (benzylic:tertiary = 1.0:1.3) prior to the comparative experiments with the targeted substrate **3c**. Our experiment gave reproducible results: 45% NMR yield and the 1.0:1.3 ratio of tertiary benzylic to primary benzylic. This reaction condition was applied to C−H azidation of **3c**.

Method III: General Procedure for Mn(salen)Cl System. According to the literature procedure,[18] a 6 mL borosilicate glass vial was charged with a magnetic stir bar, 0.6 mmol of substrate (**3b**, **3c**, or **3d**), 0.8 equivalents of iodosylbenzene (110 mg, 0.48 mmol) and 3.0 mol% Mn(salen)Cl (11 mg, 18 μmol). To the vial was added 1.0 mL of 1.5 M sodium azide solution (aq., 1.5 mmol) and ethyl acetate (1.0 mL) sequentially. The capped vial was stirred at room temperature (25 °C) until the complete consumption of iodosylbenzene. Additional 1.0 mol% Mn(salen)Cl (3.5 mg, 6.0 μmol), 1.5 M sodium azide solution (0.10 mL, 0.15 mmol), and iodosylbenzene (110 mg, 0.48 mmol) were added sequentially. The vial was recapped and stirred at room temperature (25 °C). After the consumption of iodosylbenzene, this step was repeated 6 times. The reaction was quenched with brine solution (10 mL) and the organic layer was separated from the extraction with ethyl acetate (15 mL) three times and concentrated. Regioselectivity of benzylic (**4b**,

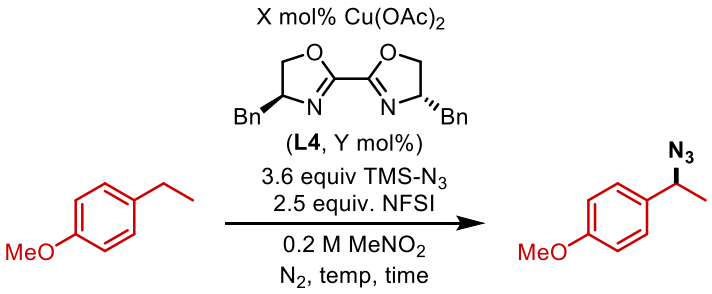
4c, or **4d**)[13,14,18] and tertiary product[12,15,16] was determined by ^{1}H NMR analysis of crude mixture with 0.6 mmol mesitylene as an external standard.

Note: (1) Salen ligand (**S1**) and manganese salen catalyst (**S2**) were synthesized according to literature procedure.[19,20] (2) Iodosylbenzene (**S3**) was synthesized according to the literature method.[21] (3) There are no literature reports for the synthesis of **4b** and **4c** using the Mn(salen)Cl system.[18] The yield of **4d** was reported but the tertiary regioisomer of **4d** was not reported.[18] (4) Since a specific procedure for each C–H substrate was not reported and the provided general procedure has a wide range of reaction time (i.e. 3-12 hours) and equivalents of reagents [i.e. repeating the addition of Mn(salen)Cl (3.5 mg, 1.0 mol%), 1.5 M sodium azide solution (0.1 mL), and iodosylbenzene (110 mg) 4-8 times] in the literature procedure, we performed the optimization of the reaction conditions for **3d** to reproduce the yield of **4d**. We obtained consistent result four times (41-46% yield, B:T = 13:1), but the reported literature yield was not achieved. Our optimal reaction condition was applied to C−H azidation of **3b**−**3d**.

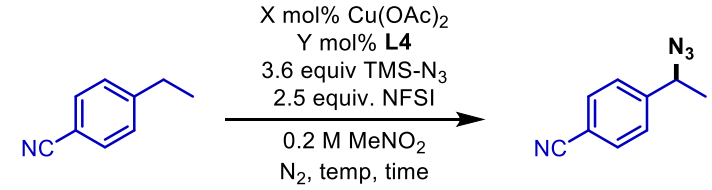
Method IV: General Procedure for Fe(OAc)$_2$·PyBOX System. According to literature procedure,[22,23] a 20 mL borosilicate glass vial was charged with a magnetic stir bar, 1.0 equivalent of $Fe(OAc)_2$ (41.7 mg, 0.24 mmol), 1.1 equivalents of 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (PyBOX, 79.6 g, 0.26 mmol), and acetonitrile (12.0 mL) sequentially in a glovebox. The resulting solution was stirred for 16 hours at room temperature (25 ℃). A 4 mL vial was charged with a magnetic stir bar, 0.2 mmol of substrate (*p*-cymene, **3a**, **3b**, or **3c**), and 3.0 equivalents of the azidation reagent **S6** (173 mg, 0.6 mmol), and the prepared 0.02 M stock solution of $Fe(OAc)_2$·PyBOX catalyst (1.0 mL). The vial was capped and taken out of the glovebox. After stirring at 50 ℃ for 48 hours, ethyl acetate (2 mL) was added to the crude solution. The solution was filtered through a basic alumina plug for ^{1}H NMR analysis.

Note: (1) **S6** was prepared in three-step synthesis including syntheses of intermediates (**S4** and **S5**) according to the literature method,[24] and stored in a glovebox. (2) The synthesis of **4b**, **4c**, and **4d** has not been previously attempted using the $Fe(OAc)_2$·PyBOX system.[22,23] (3) *p*-Cymene was chosen as the substrate to reproduce the reported yield (70%, isolated yield)[23] and the ratio of regioisomers (tertiary benzylic:primary benzylic = 14:1)[23] prior to the comparative experiments with the targeted substrates **3b**-**3d**. Our experiment gave the reproducible result (82% NMR yield and the 14.1:1.0 ratio of tertiary to primary by ^{1}H NMR analysis). This reaction condition was applied to the C−H azidation of **3b**−**3d**.

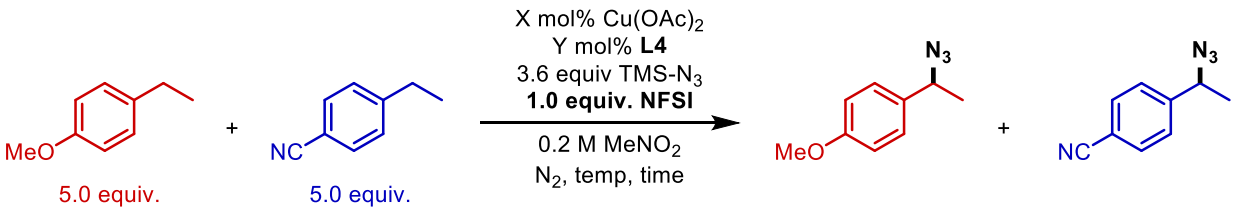
6. Reactivity Assessment



Condition A	conv. = 100%	**45%**
Condition B (Standard)	conv. = 76%	**74%**
Condition C	conv. = 91%	**81%**



Condition A	conv. = 61%	**25%**
Condition B (Standard)	conv. = 15%	**12%**
Condition C	conv. = 29%	**20%**



Condition A	**86%**	**2.9%**
Condition B (Standard)	**94%**	**3.2%**
Condition C	**96%**	**3.3%**

Condition A. 2.0 mol% $Cu(OAc)_2$, 4.0 mol% **L4**, **50 °C, 16 h**

Condition B. 2.0 mol% $Cu(OAc)_2$, 4.0 mol% **L4**, 30 °C, 24 h **(Standard Condition)**

Condition C. 6.0 mol% $Cu(OAc)_2$, 12 mol% L4, 30 °C, 24 h

* NFSI was the limiting reagent.
* Yield (%) was based on the mole of NFSI.

Figure S2. Independent comparison and competition experiments of *p*-methoxy and *p*-cyanoethylbenzene. Reaction conditions for screening were adopted from General Procedure A.

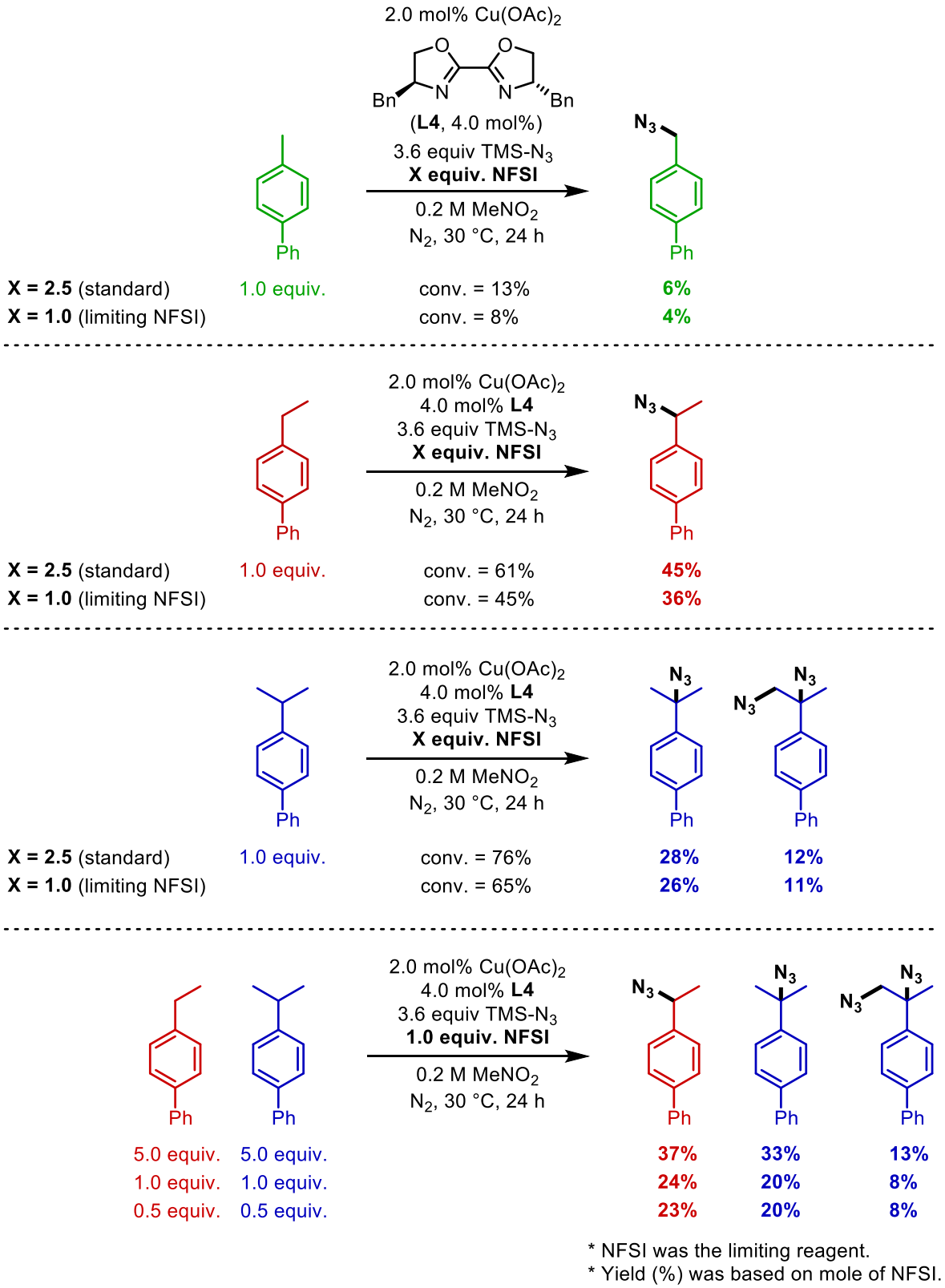


Figure S3. Independent comparison and competition experiments of primary, secondary, and tertiary benzylic C–H substrate. Reaction conditions for screening were adopted from General Procedure A.

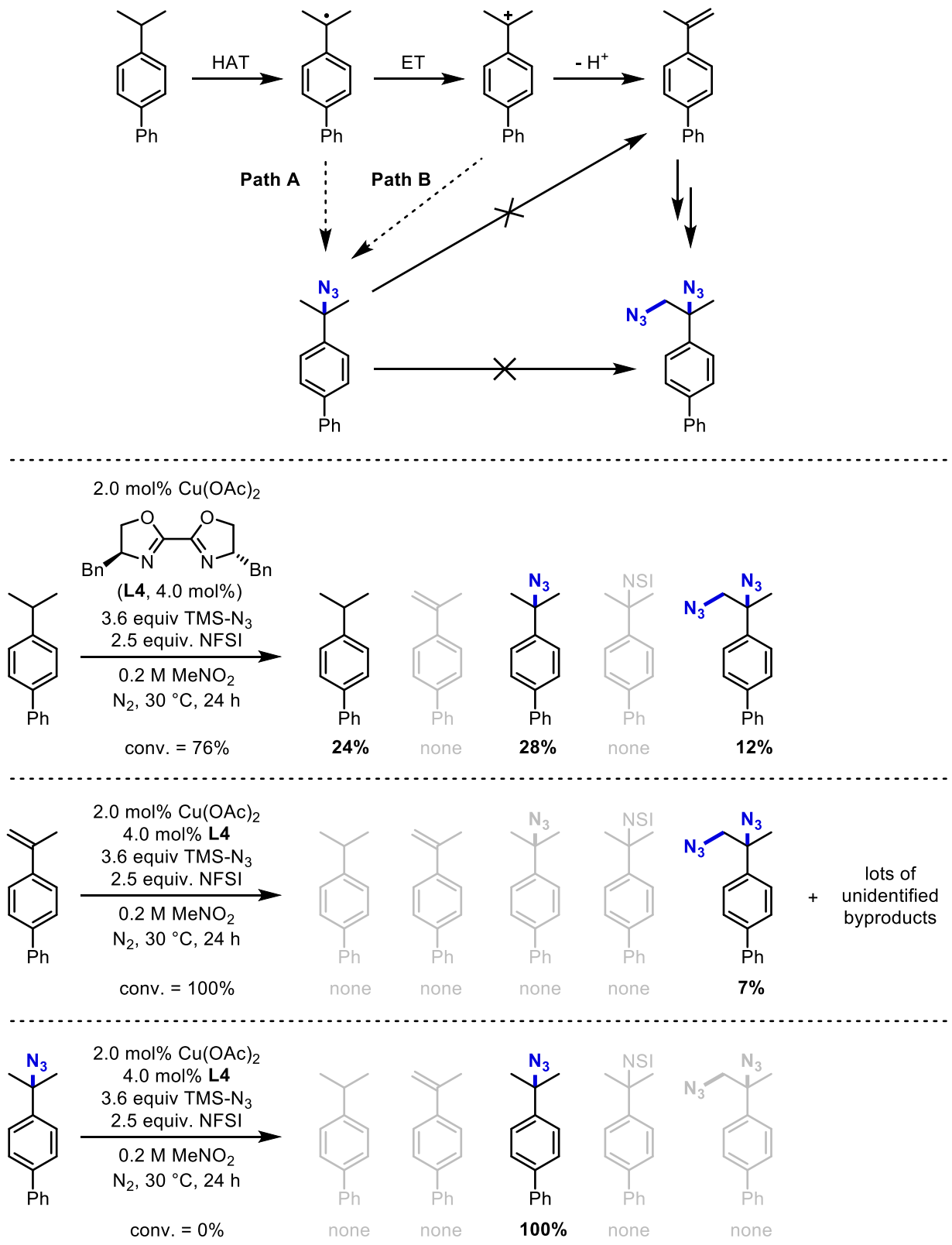
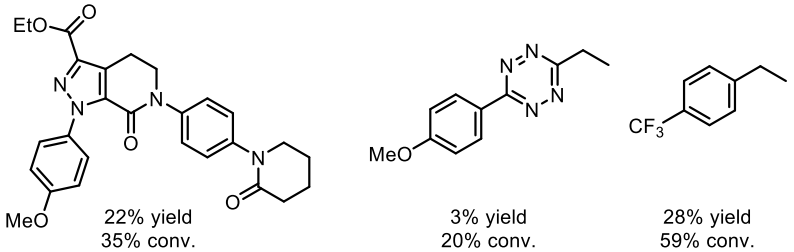


Figure S4. Investigation of vicinal diazide formation. Reaction conditions for screening were adopted from General Procedure A.

Table S13. Unsuccessful C–H Substrates

A

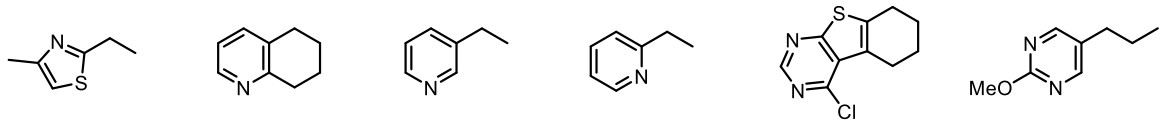


22% yield
35% conv.

3% yield
20% conv.

28% yield
59% conv.

B



not found
100% conv.

not found
100% conv.

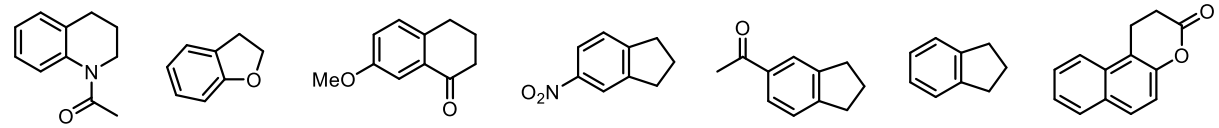
not found
82%conv.

not found
63% conv.

9% yield
100% conv.

9% yield
84% conv.

C



21% yield
100% conv.

31% yield
100% conv.

9% yield
83% conv.

18% yield
100% conv.

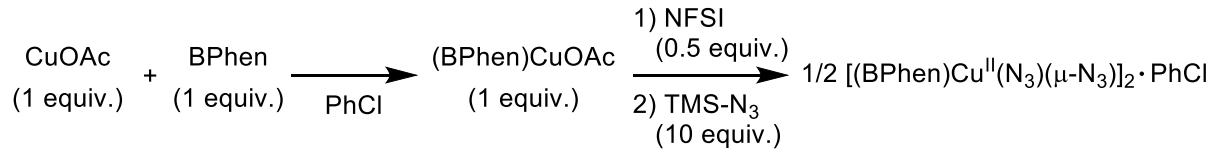
6% yield
100% conv.

12% yield
100% conv.

Splitomicin
24% yield
100% conv.

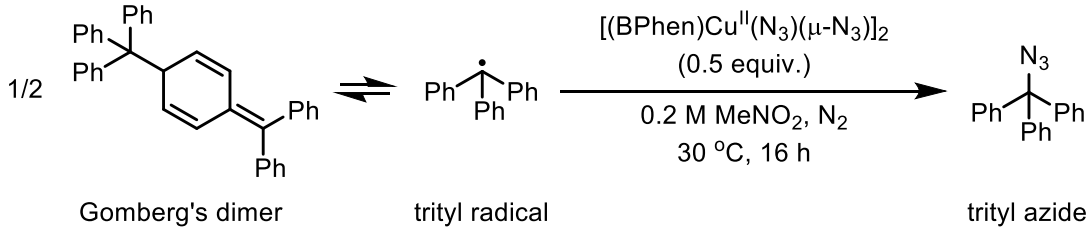
Some substrates were not successful for azidation. Electron-deficient heterobenzylic and benzylic substrates gave poor conversion (Table S13A). Despite of good to excellent conversion, thiazole, pyridine, purimidine derivatives gave low-to-negligible yield (Table S13B). In Table S13C, *N*-acetyl protected 1,2,3,4-tetrahydroquinoline gave lower yield in comparison to *N*-sulfonyl protected compound (42%, **4ac** in Table 2 in the manuscript). Dihydrobenzofuran, dihydronaphthalenone, and indane derivatives showed high conversion but low yield. More than 50% yield of elimination product was observed in the reaction of splitomicin.

7. Preparation, Crystallization and Reaction of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2$



Preparation and Crystalization of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2$: A 4 mL borosilicate glass vial was charged with copper(I) acetate (7.4 mg, 60 μmol) and 1.0 equivalent of bathophenanthroline (20 mg, 60 μmol), and a magnetic stir bar outside a glovebox. The vial was capped with an open-top cap installed with a TFE lined silicone SURE-LINK™ septum. The septum cap was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the vial was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the vial was taken out of the glovebox. Chlorobenzene (3.0 mL, 20 μM) was then added to the vial through the cap and the reaction mixture was stirred at room temperature (25 ℃) for 30 minutes, the solution was cannulated into the vial charged with 0.50 equivalents of *N*-fluorobenzenesulfonimide (9.5 mg, 30 μmol) and a magnetic stir bar. After stirring, 10 equivalents of azidotrimethylsilane (80 μL, 0.60 mmol) was added to the solution. The resulting solution was stirred for 10 minutes and left with no agitation for 24 hours. Resulting dark green crystals were washed with pentane (5 mL x 12 times) to afford 21 mg of 1/2 $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$ in 65% yield. Elemental analysis (E.A.) and X-ray crystallography were performed for characterization of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$.

E.A. (%): Calcd. For $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$ ($C_{54}H_{37}ClCu_2N_{16}$, 1072.52 g/mol) C, 60.47; H, 3.48; N, 20.90; Found. C, 59.67; H, 3.59; N, 20.67.



Reaction of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$ with 3-triphenylmethyl-6-diphenylmethylidene-1,4-cyclohexadiene (Gomberg's dimer): A 4 mL borosilicate glass vial was charged with 3-triphenylmethyl-6-diphenylmethylidene-1,4-cyclohexadiene (7.3 mg, 15 μmol; 30 μmol of trtyl radical), 0.5 equivalent of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$ (16 mg, 15 μmol), and a magnetic stir bar inside a glovebox. The vial was capped with an open-top cap installed with a TFE lined silicone SURE-LINK™ septum and taken out of the glovebox. Nitromethane (0.15 mL, 0.20 M) was then added into the vial through the cap and the reaction mixture was stirred and heated to 30 ℃ (inner temperature) in a heating block on a hot plate. After 16 hours, the reaction mixture was cooled to room temperature (25 ℃). All precipitates and catalysts were filtered out through a pipette-silica plug with dichloromethane (1.0 mL x 3 times). The yield (91%) of trityl azide was determined by ^1H NMR analysis of crude mixture with 0.2 mmol mesitylene as an external standard. After evaporation of solvent on a rotary evaporator at 30 ℃, flash column chromatography was performed. The isolated compound was dried to give 7.4 mg (86% isolated yield) of trityl azide. The ^1H and ^{13}C NMR spectra of trityl azide match the literature report.[25,26]

8. Crystallographic Data for $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$.

Data Collection

A green crystal with approximate dimensions 0.09 x 0.05 x 0.01 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[27]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 20 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 5489 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 22580 data were harvested by collecting 4 sets of frames with 0.5º scans in ω and φ with exposure times of 70 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[28]

Structure Solution and Refinement

The diffraction data were consistent with the space groups $P\bar{1}$ and $P1$. The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.[29-34]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The dinuclear Cu complex occupies a crystallographic inversion center, thus only one half of the complex is symmetry-independent.

There is also one solvent molecule of chlorobenzene per dinuclear complex. The solvent molecule is disordered over a crystallographic inversion center. The refinement of the solvent molecule was problematic: whereas it was possible to locate all carbon atoms, the chlorine atom was refined with a total occupancy of 71.8(6)% (or 35.9(3) % in the asymmetric unit). This result is believed to be due to the solvent molecule disorder but it was not possible to locate alternative Cl atom positions. The solvent molecule composition is consistent with the synthetic procedure and a possible benzene/chlorobenzene compositional disorder was ruled out. The solvent molecule was refined with an idealized geometry[35] and thermal displacement parameter restraints.[30]

The final least-squares refinement of 347 parameters against 6999 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0420 and 0.1075, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{54}H_{37}ClCu_2N_{16}$ (M =1072.52 g/mol): triclinic, space group P-1 (no. 2), a = 6.452(2) Å, b = 12.895(4) Å, c = 14.135(5) Å, α = 88.073(16)°, β = 80.255(12)°, γ = 81.571(17)°, V = 1146.4(7) Å^3, Z = 1, T = 100.01 K, μ(MoKα) = 1.046 mm^{-1}, $Dcalc$ = 1.554 g/cm^3, 22580 reflections measured (2.924° ≤ 2Θ ≤ 61.16°), 6999 unique (R_{int} = 0.0424, R_{sigma} = 0.0515) which were used in all calculations. The final R_1 was 0.0420 (I > 2σ(I)) and wR_2 was 0.1075 (all data).

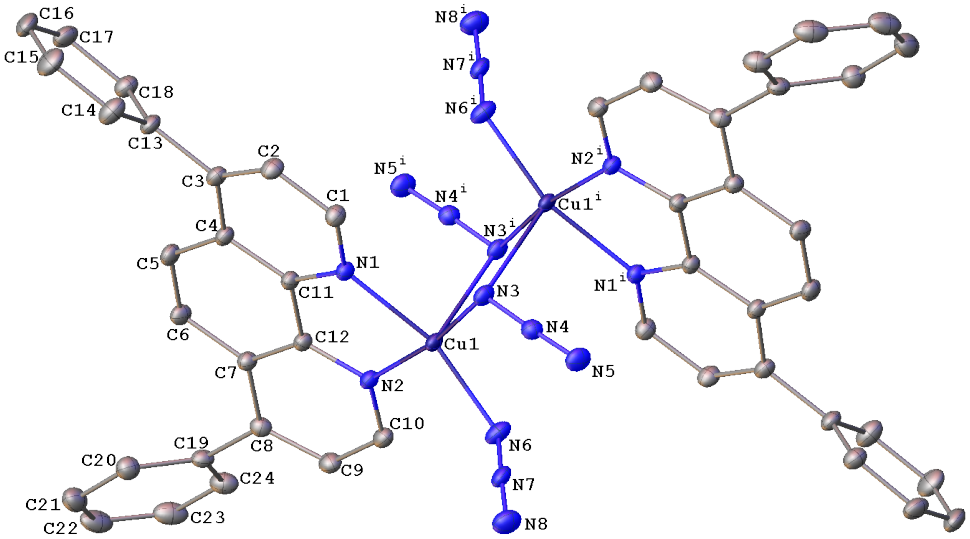


Figure S5. A molecular drawing of the entire complex in [(BPhen)Cu^{II}(N_3)(μ-N_3)]$_2$ · PhCl shown with 50% probability ellipsoids. All H atoms and solvent molecule are omitted. [Symmetry code: (i) 2−x, 2−y, 1−z.]

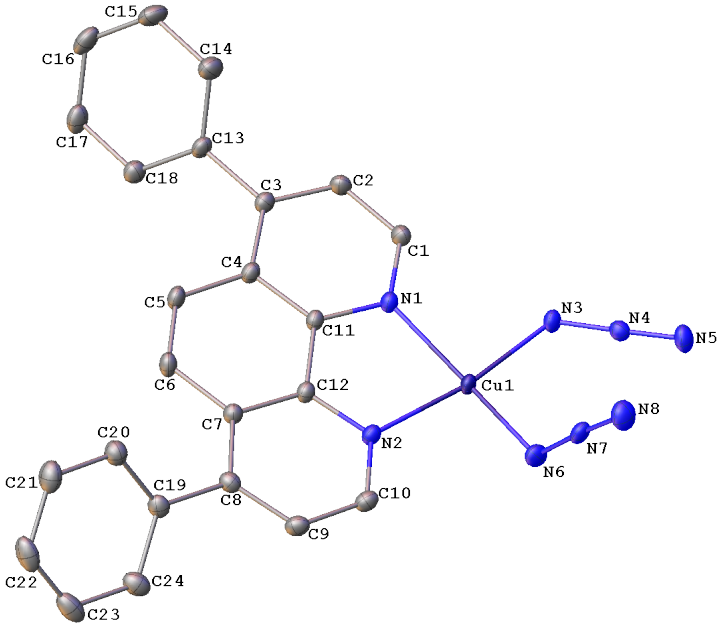


Figure S6. A molecular drawing of the symmetry independent portion of the complex in [(BPhen)Cu^{II}(N_3)(μ-N_3)]$_2$ · PhCl shown with 50% probability ellipsoids. All H atoms and solvent molecule are omitted.

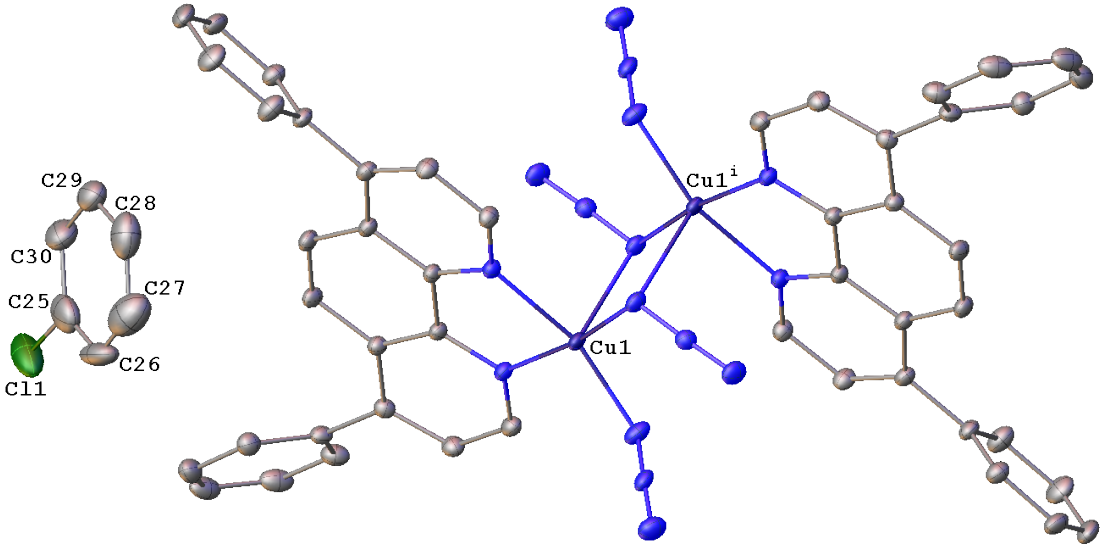


Figure S7. A molecular drawing of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$ shown with 50% probability ellipsoids. All H atoms are omitted. [Symmetry code: (i) 2−*x*, 2−*y*, 1−*z*.]

Table S14. Crystal Data and Structure Refinement for $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2 \cdot PhCl$.

Empirical formula	$C_{48}H_{32}Cu_2N_{16} \cdot C_6H_5Cl$
Formula weight	1072.52
Temperature/K	100.0
Crystal system	triclinic
Space group	$P\overline{1}$
a/Å	6.452(2)
b/Å	12.895(4)
c/Å	14.135(5)
α/°	88.073(16)
β/°	80.255(12)
γ/°	81.571(17)
Volume/Å^3	1146.4(7)
Z	1
ρ_{calc}g/cm^3	1.554
μ/mm^{-1}	1.046
F(000)	548.0
Crystal size/mm^3	0.09 × 0.05 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.924 to 61.16
Index ranges	$-9 \le h \le 9$, $-18 \le k \le 18$, $-15 \le l \le 20$
Reflections collected	22580
Independent reflections	6999 [R_{int} = 0.0424, R_{sigma} = 0.0515]
Data/restraints/parameters	6999/36/347
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0605, wR_2 = 0.1075
Largest diff. peak/hole / e Å^{-3}	0.69/-0.48

9. Experimental and Computational Redox Potentials and Reaction Energetics

Cyclic Voltammetry (CV) of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2$: CV experiments were performed with BASi potentiostat and cell stand at room temperature under nitrogen gas. A glassy carbon (1.5 mm diameter) as working electrode was polished with alumina before each experiment. An $Ag/AgNO_3$ reference electrode and Pt wire counter electrode were used. The $Ag/AgNO_3$ was calibrated with ferrocene in the same concentration (0.23 mM in nitromethane) as analyte. The supporting electrolyte for all electrochemical experiments was 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP). The solution of 0.23 mM Cu complex and 0.1 M TBAHFP in nitromethane was used to measure the half-wave potentials $E^{\circ}_{1/2}(Cu^{II|I})$ with 50 mV/s scan rate.

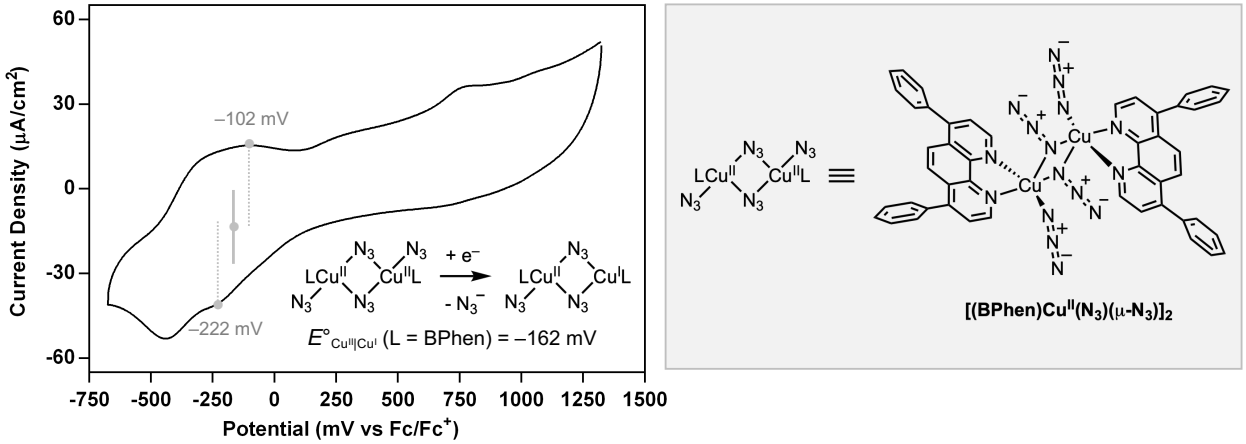


Figure S8. Cyclic voltammogram of $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2$.

Electronic Structure of the $[LCu^{II}(N_3)_2]_2$ Dimer and Analysis of the Dimer/Monomer Equilibrium.

Electronic structure of the experimentally isolated $[LCu^{II}(N_3)_2]_2$ dimer (*L* = BPhen experimentally and *L* = Phen computationally) was probed at the DFT level. Dimerization in the triplet electronic state was found to be energetically most favorable, the triplet dimer being ~7.7 kcal/mol lower in free energy relative to the corresponding infinitely separated monomers. When the ligand is switched to the chiral BiOx* (**L4**) ligand, however, the dimer stabilization is reduced to only ~2.0 kcal/mol.

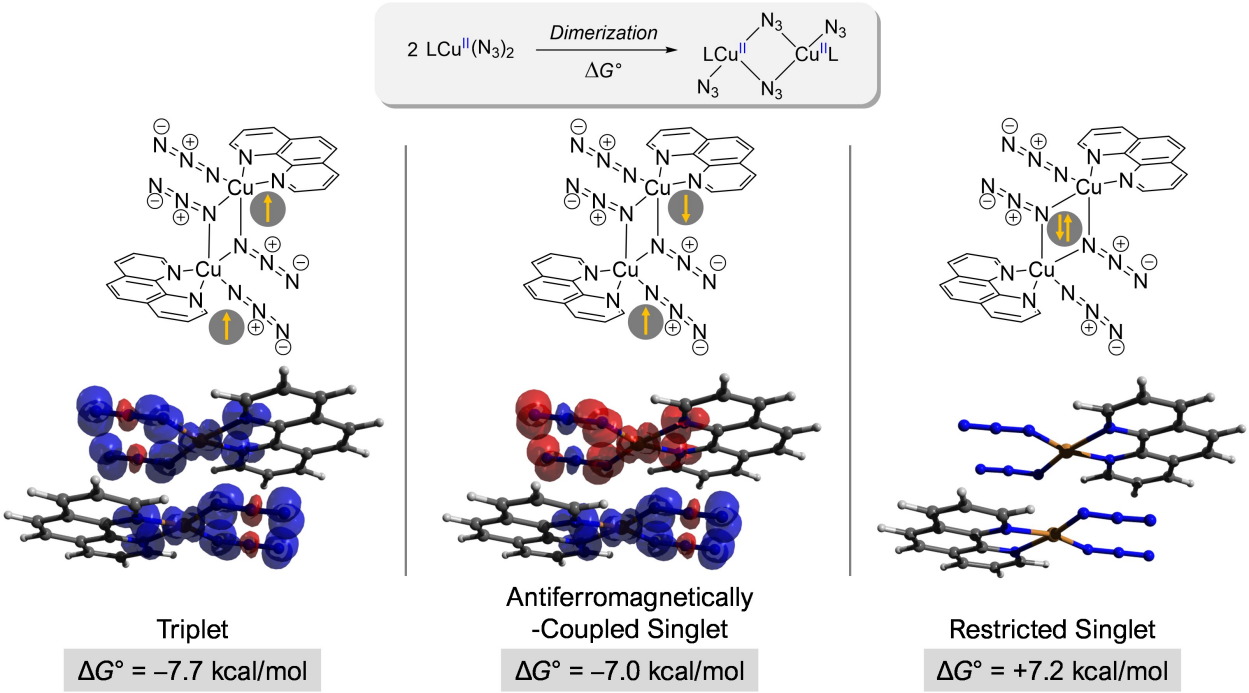


Figure S9. Gibbs free energy change (kcal/mol) due to dimerization. Calculations done at 298.15 K at M06-L/basis-II/SMD($MeNO_2$)//B3LYP-D3(BJ)/basis-I level of theory.

Energetics for Reactivity and Redox Potential Calculations

Table S15. Solution phase electronic energies, E(sol)/hartree, spin-projected electronic energies, E'(sol)/hartree, thermal contribution to Gibbs free energy/hartree and absolute solution-phase Gibbs free energies, G(sol)/hartree (at 298.15 K) computed at M06-L/basis-II/SMD(nitromethane) //B3LYP-D3(BJ)/basis-I level of theory.

File Description	E(sol)/a.u.	E'(sol)/a.u. (Spin-projected)	Thermal Contribution to *G*/a.u.	*G*(sol)/a.u. (T=298.15K)
Phen-[Cu(i)(N3)]-Singlet	-932.0027411		0.142544	-931.8571771
Phen-[Cu(ii)(N3)2]-Doublet	-1096.264552		0.151653	-1096.109879
Phen-[Cu(ii)(N3)2]2-Triplet	-2192.566919		0.331833	-2192.232066
Phen-[Cu(ii)(N3)2]2-afc-singlet	-2192.566875	-2192.566876	0.332864	-2192.230992
Phen-[Cu(ii)(N3)2]2-restricted-singlet	-2192.541209		0.329961	-2192.208228
Phen-[Cu(ii)(N3)2][Cu(i)(N3)]-Doublet	-2028.300921		0.320247	-2027.977654
BPhen-[Cu(i)(N3)]-Singlet	-1394.21454		0.292941	-1393.918579
BPhen-[Cu(ii)(N3)2]-Doublet	-1558.478141		0.301591	-1558.17353
BPhen-[Cu(ii)(N3)2]2-Triplet	-3116.994757		0.633514	-3116.358223
BPhen-[Cu(ii)(N3)2][Cu(i)(N3)]-Doublet	-2952.734291		0.626283	-2952.104988
BioxBn-[Cu(i)(N3)]-Singlet	-1394.613896		0.322542	-1394.288334
BioxBn-[Cu(ii)(N3)2]-Doublet	-1558.869798		0.331684	-1558.535094
BioxBn-[Cu(ii)(N3)2]2-Triplet	-3117.76763		0.691206	-3117.073404
BioxBn-[Cu(ii)(N3)2][Cu(i)(N3)]-Doublet	-2953.507024		0.680222	-2952.823782
N3(-)Anion	-164.381172		-0.005329	-164.383481
PhCH(+)Me	-310.141482		0.113942	-310.02452
PhCH(.)Me	-310.3025969		0.11053	-310.1890469
PhC(+)Me2	-349.4749839		0.138991	-349.3329729
PhC(.)Me2	-349.6287683		0.13643	-349.4893183
1-Naph-CH(+)Me	-463.8239193		0.157228	-463.6636713
1-Naph-CH(.)Me	-463.9820586		0.154009	-463.8250296
INT-R-formal-Cu(iii)(N3)2(Naph)	-2022.866549		0.518644	-2022.344885
INT-S-formal-Cu(iii)(N3)2(Naph)	-2022.871457		0.517816	-2022.350621
RE-TS1-R-Cu(iii)(N3)2(Naph)	-2022.857459		0.516226	-2022.338213
RE-TS1-S-Cu(iii)(N3)2(Naph)	-2022.859985		0.51711	-2022.339855
TS2-b3-R-BioxDimer-Naph-RAL	-3581.769096	-3581.770596	0.873308	-3580.894268
TS2-b3-S-BioxDimer-Naph-RAL	-3581.764865	-3581.766271	0.873066	-3580.890185
TS2-b1-R-BioxDimer-Naph-RAL	-3581.758769	-3581.758602	0.873644	-3580.881938
TS2-b1-S-BioxDimer-Naph-RAL	-3581.756309	-3581.756889	0.872568	-3580.881301
TS2-t3-R-BioxDimer-Naph-RAL	-3581.762928	-3581.764806	0.870997	-3580.890789
TS2-t3-S-BioxDimer-Naph-RAL	-3581.767102	-3581.7689	0.871279	-3580.894601
TS2-t1-R-BioxDimer-Naph-RAL	-3581.766474	-3581.767069	0.871371	-3580.892678
TS2-t1-S-BioxDimer-Naph-RAL	-3581.768039	-3581.76929	0.872504	-3580.893766

Computed Reduction Potentials

Accurate computational prediction of standard reduction potentials for copper-containing compounds using density functional methods can sometimes prove challenging.[36] In this work, we have computed absolute reduction potentials for various species and used two sets of correction factors, f(Cu) [= 3.706 V] for copper-based complexes and f(Org) [= 4.487 V] for organic species, to convert computed reduction potentials into values relative to the $Fc|Fc^+$ reference used experimentally. The values of the correction factors are taken as those required to map the computed absolute reduction potentials for $[LCu^{II}(N_3)_2]_2$ (*L* = BPhen) dimer species and ethylbenzene cation to their experimental values (Figure S8 and Table S16). Thus, reported values for *other* copper-containing or organic molecules rely on computation to predict a *variation* from the reference compounds, not a first-principles reduction potential.

Specifically, using the reaction in eq S3 and *L* = BPhen, the absolute reduction potential for Cu^{II}/Cu^{I} system was calculated to be 3.544 V at the M06-L/basis-II/SMD(nitromethane)//B3LYP-D3(BJ)/basis-I level of theory (298.15 K). Experimentally, the corresponding value versus the $Fc|Fc^+$ reference potential was determined to be –0.162 V. Thus, we have used f(Cu) = (3.544 + 0.162) V = 3.706 V for computing reduction potentials of all copper-based complexes.

Similarly, the reaction in eq S4 was used to determine the correction factor, f(Org). The absolute reduction potential for the $R^+|R^\bullet$ couple (*R* = PhCHMe) was computed to be 4.477 V at 298.15 K, while the corresponding experimental value was determined to be –0.01 V.[37] Thus, we have used f(Org) = (4.477 + 0.01) V = 4.487 V for computing reduction potentials of the other organic radicals.

Note that in both cases, the correction factor f needs to be ***subtracted*** from the computed absolute reduction potential to obtain values relative to the $Fc|Fc^+$ reference.

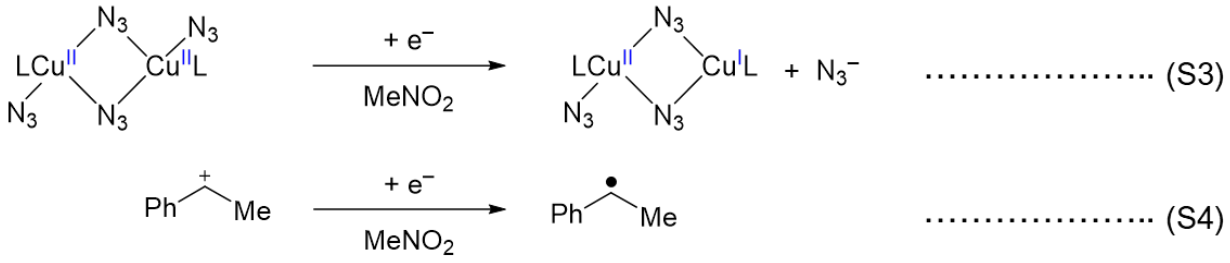
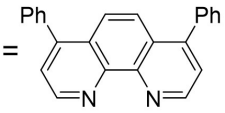
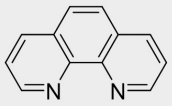
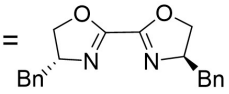
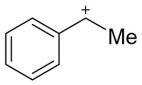
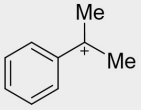
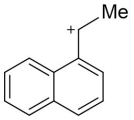


Table S16: Calculated (vs $Fc^{0/+}$), and experimental (vs $Fc^{0/+}$) reduction potentials (V) of various species at 298.15 K using reaction schemes (eqs S3 and S4).

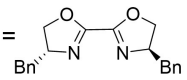
f(Cu) = 3.706 V			
$[LCu^{II}(N_3)_2]_2$ Species	$E°$ (Cu^{II}|Cu^{I}) [a] absolute, V	$E°$ (Cu^{II}|Cu^{I}) vs $Fc^{0/+}$, V	$E°$ (Cu^{II}|Cu^{I}) [*exp*] vs $Fc^{0/+}$, V
L = 	3.544	–0.162	–0.162 [b]
L = 	3.482	–0.223	*N.A.*
L = 	3.642	–0.063	*N.A.*
f(Org) = 4.487 V			
R^+ Species	$E°$ (R^+|$R^•$) [a] absolute, V	$E°$ (R^+|$R^•$) vs $Fc^{0/+}$, V	$E°$ (R^+|$R^•$) [*exp*] vs $Fc^{0/+}$, V
	4.477	–0.01	–0.01 [c]
	4.254	–0.233	–0.22 [c]
	4.391	–0.096	*N.A.*

[a]Computed at 298.15 K at M06-L/basis-II/SMD(nitromethane)//B3LYP-D3(BJ)/basis-I level of theory. [b]Half-wave potentials $E°_{1/2}(Cu^{II|I})$ was measured; Glassy carbon (W.E.), Pt wire (C.E.), $Ag/AgNO_3$ (R.E.), 50 mV/s scan rate, 0.23 mM $[(BPhen)Cu^{II}(N_3)(\mu\text{-}N_3)]_2$, 0.1 M TBAHFP (electrolyte), rt, N_2. [c]Ref. 37.

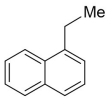
Thermodynamics of Radical Polar Crossover Pathway

Using the reduction potentials presented in Table S16, Gibbs free energy change (ΔG°) for the oxidation of the $R^\bullet$ radical (*R* = 1-Naph(CH)Me) by the Cu^{II} dimer yielding the R^+ cation can be calculated as follows:

E° ($Cu^{II}|Cu^{I}$) = –0.063 V

L = 

E° ($R^+|R^\bullet$) = –0.096 V

R = 

E° (overall-reaction) = (0.096 – 0.063) V = 0.033 V

ΔG° (overall-reaction) = – nFE° (overall-reaction)
= – 1 × 23.061 × 0.033 kcal/mol
= – 0.8 kcal/mol

Scheme S1. Derivation of Gibbs free energy change (ΔG°) for the oxidation of the 1-Naph-CH(•)Me radical by the Cu^{II}-dimer yielding the corresponding benzylic cation. Reduction potentials were obtained from Table S16.

Comparison of Product Forming Pathways

As discussed in the text, starting from the 1-Naph-CH(•)Me and $[LCu^{II}(N_3)_2]_2$ (*L* = **L4**) dimer, we have considered three possible pathways leading to the product [1-Naph-CH(N_3)Me] formation. These pathways are detailed in Figure S10, and their corresponding energetics are shown in Figure S11.

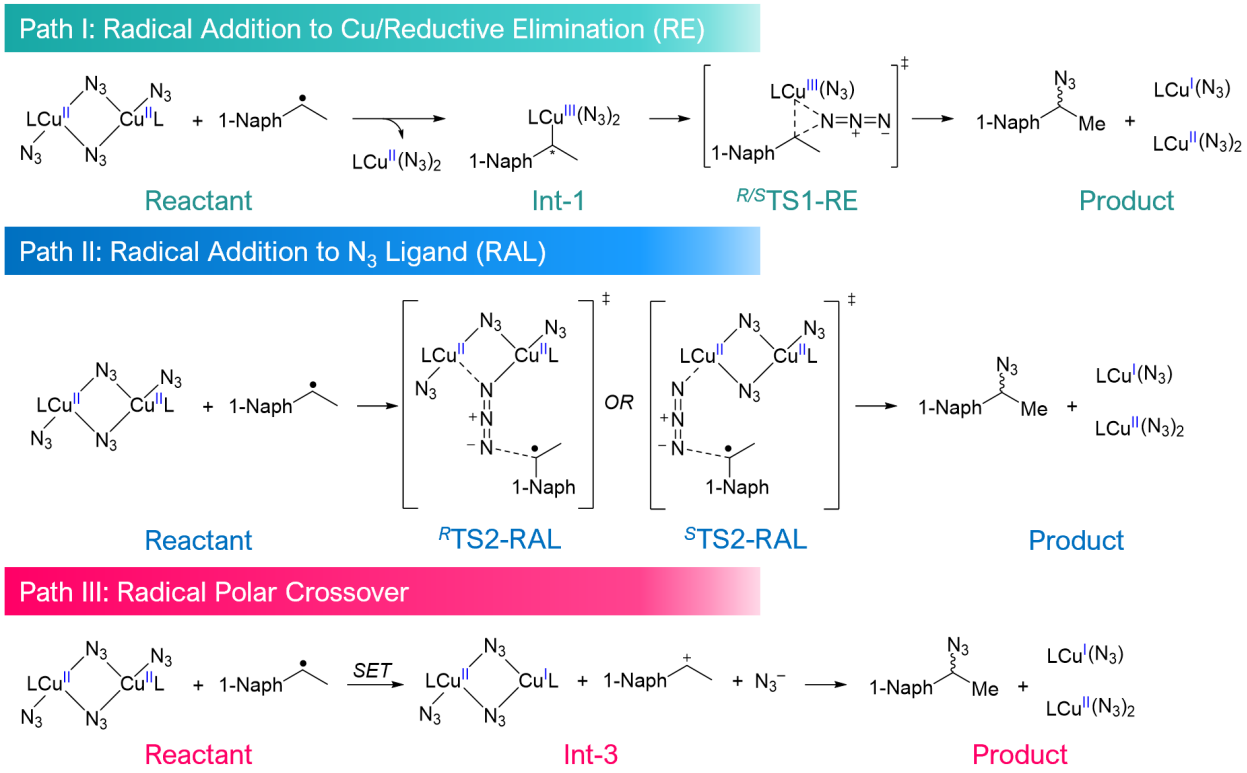


Figure S10. Possible pathways leading to the benzylic azide formation.

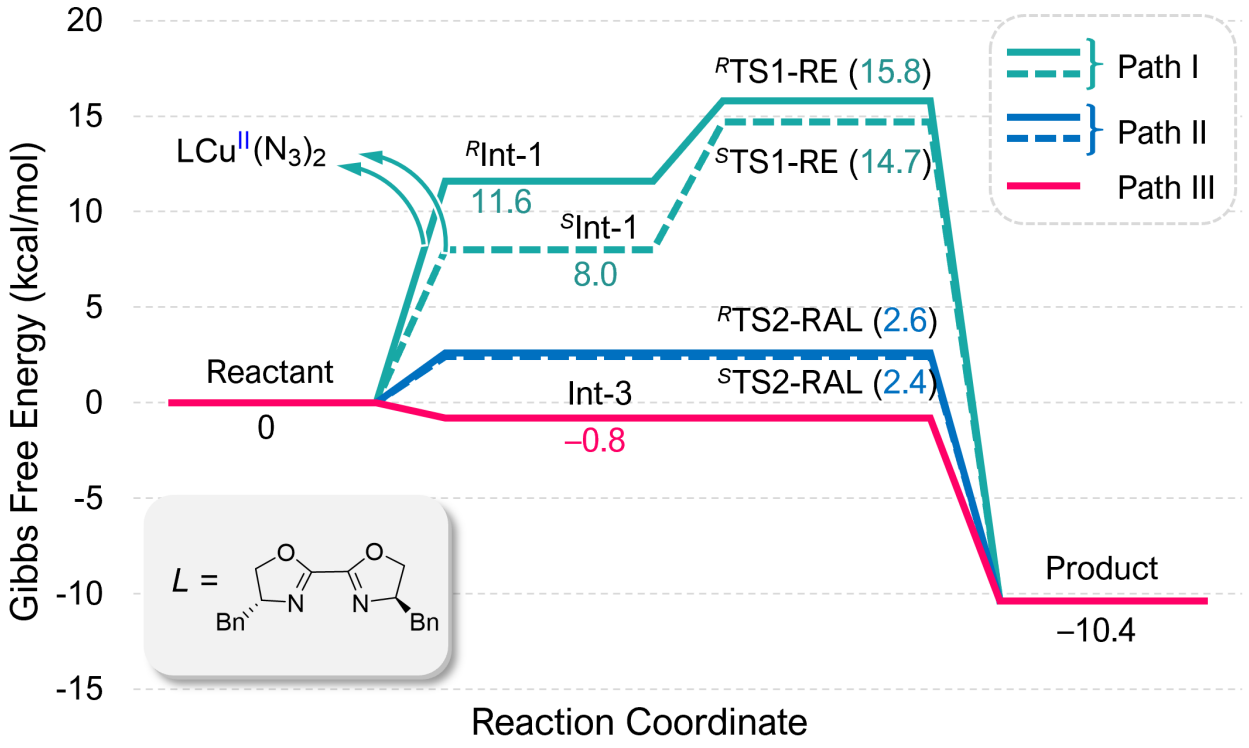


Figure S11. Energetics of pathways leading to the benzylic azide formation using the BiOx (**L4**) ligand. Gibbs free energies are in kcal/mol computed at 298.15 K at M06-L/basis-II/SMD($MeNO_2$)//B3LYP-D3(BJ)/basis-I level of theory. Free energy of **Int-3** was determined according to Scheme S1.

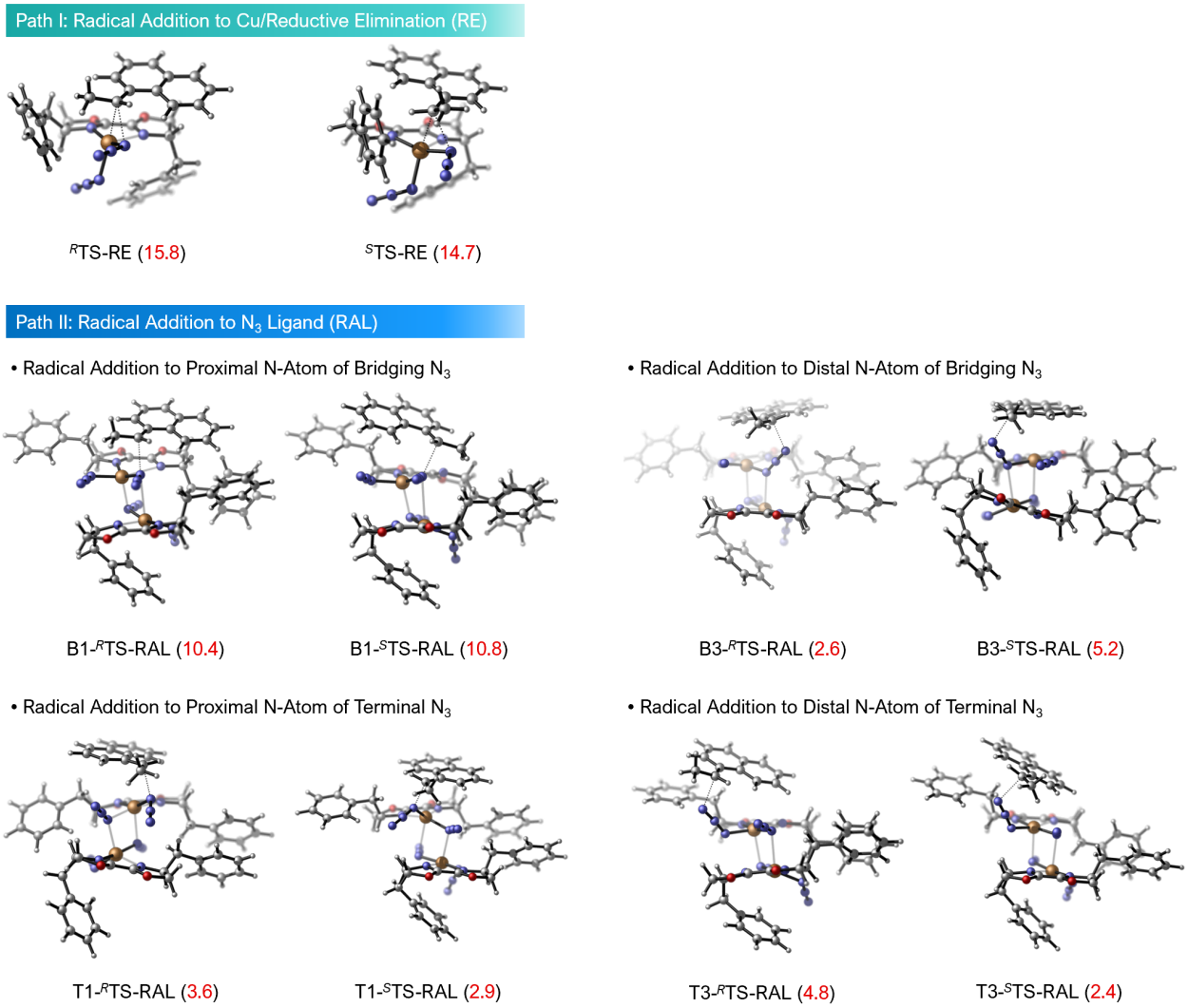
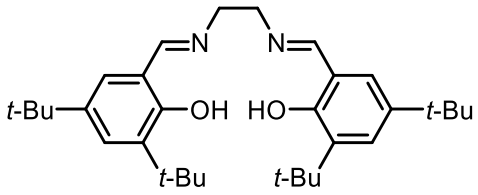


Figure S12. Optimized transition-state (TS) structures leading to product formation via reductive elimination (RE) and direct radical addition to the azide ligand (RAL) for both pro-*R* and pro-*S* faces of the benzylic radical derived from 1-ethylnaphthalene. Gibbs free energies of activation ($\Delta G^{\ddagger}$; kcal/mol) of the respective TS structures are included in parenthesis. Gibbs free energies are reported at 298.15 K calculated at M06-L/basis-II/SMD($MeNO_2$)//B3LYP-D3(BJ)/basis-I level of theory. "RE" implies reductive elimination (Path-I). The prefix "B3–" implies that the reaction is happening at the distal *N*-atom of the bridging azide group. Similarly, "T1–" prefix means that it is the proximal *N*-atom of the terminal azide group.

10. Characterization Data



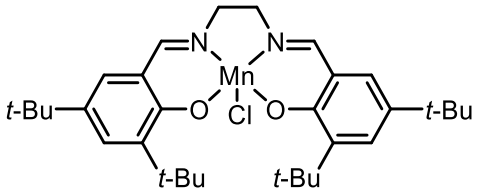
S1

6,6'-((1*E*,1'*E*)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-di-tert-butylphenol) (S1): Prepared according to the literature procedure. A 250 mL round-bottle flask was charged with a magnetic stir bar, 2.3 equivalents of 3,5-di-*t*-butylsalicylaldehyde (2.1 g, 9.0 mmol) and ethanol (80 mL). To the solution, 1,2-diaminoethane (0.27 mL, 4.0 mmol) was added dropwise. The resulting solution was heated under reflux for 12 hours and cooled to 0 ℃ for 2 hours. The yellow precipitate was filtered and washed with cold ethanol (30 mL) to afford 1.72 g of **S1**. ^{1}H NMR spectrum of **S1** was matched with the literature.[19]

Isolated Yield: 87%

Physical Property: Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 13.64 (s, 2H), 8.38 (s, 2H), 7.36 (d, 2H, J = 2.5 Hz), 7.06 (d, 2H, J = 2.5 Hz), 3.92 (s, 4H), 1.43 (s, 18H), 1.28 (s, 18H).



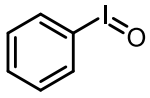
S2

Manganese salen catalyst (S2): Prepared from **S1** according to the literature procedure.[20] A 250 mL three-neck round-bottle flask was charged with a magnetic stir bar, 3.0 equivalents of manganese(II) acetate tetrahydrate (9.0 mmol, 2.2 g) and ethanol (60 mL) under nitrogen gas and heated under reflux. To the solution, a solution of **S1** (3.0 mmol, 1.5 g) in toluene (45 mL) was added dropwise. After 2 hours, air bubbling to the solution through a needle was performed for 1 hour. Brine solution (80 mL) was added and the resulting solution was cooled to room temperature (25 ℃). The needle was detached and toluene (25 mL) was added to the reaction mixture. The solution was washed with water (120 mL) three times and brine solution (100 mL) three times sequentially. The organic layer was dried and concentrated to afford 1.6 g of **S2**. HRMS analysis was performed for characterization of **S2**.

Isolated Yield: 92%

Physical Property: Brown solid.

HRMS (ESI) calculated for $C_{32}H_{46}ClMnN_2O_2^-$ $[M]^-$ 580.2634, found 580.2636.



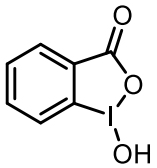
S3

iodosylbenzene (S3): Prepared according to the literature procedure.[21] 3.0 M aqueous sodium hydroxide solution (55 mL) was added dropwise to (diacetoxyiodo)benzene (10 g, 31 mmol) over 10 minutes. After stirring 2 hours at room temperature (25 ℃), the resulting solid was washed with water (100 mL) twice and chloroform (125 mL) twice sequentially and dried in vacuo to afford 5.1 g of **S3**. ^{1}H NMR spectrum of **S3** was matched with the literature.[21]

Isolated Yield: 75%

Physical Property: Colorless solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.08 – 8.02 (m, 2H), 7.64 – 7.55 (m, 2H).



S4

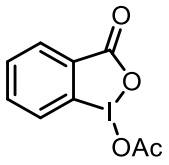
1-hydroxy-1,2-benziodoxol-3(1*H*)-one (S4): Prepared according to the literature procedure.[24] A 100 mL round-bottom flask was charged with a magnetic stir bar, 1.00 equivalents of 2-iodobenzoic acid (6.40 g, 260 mmol) and 30% v/v aqueous acetic acid (50 mL). 1.15 equivalents of $NaIO_4$ (6.40 g, 300 mmol) was added to the solution at room temperature (25 ℃) and the reaction mixture was heated to 120 ℃. After 4 hours, the solution was cooled to room temperature (25 ℃) and quenched with water (180 mL). The precipitate was filtered, washed with water (20 mL) three times and cold acetone (20 mL) three times sequentially, and dried *in vacuo* to give 6.1 g of **S4**. ^{1}H NMR spectrum of **S4** was matched with the literature.[24]

Isolated Yield: 90%

Physical Property: Colorless crystal.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (s, 1H), 8.02 (dd, J = 7.6, 1.5 Hz, 1H), 7.97 (ddd, J = 8.6, 7.2, 1.5 Hz, 1H), 7.85 (dd, J = 8.2, 1.0 Hz, 1H), 7.71 (td, J = 7.2, 1.0 Hz, 1H).

Note: Residual $NaIO_4$ should be washed thoroughly with additional water/cold acetone until ^{1}H NMR analysis proves nearly 100% purity of **S4** with external standard.



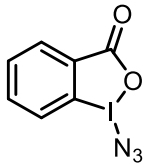
S5

1-(acetyloxy)-1,2-benziodoxol-3(1*H*)-one (S5): Prepared from **S4** according to the literature procedure.[24] To a 50 mL round-bottom flask charged with a magnetic stir bar, **S4** (3.0 g, 11 mmol) was added acetic anhydride (11 mL) at room temperature (25 ℃). The cloudy solution was heated to 135 ℃ and stirred until the solution becomes clear. The reaction mixture was cooled to –20 ℃ and stayed for 1 hour. The grown crystals were filtered, washed with pentane three times, and dried in vacuo to afford 3.3 g of **S5**. ^{1}H NMR spectrum of **S5** was matched with the literature.[24]

Isolated Yield: 98%

Physical Property: Colorless crystal.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.94 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.73 (td, *J* = 7.4, 1.0 Hz, 1H), 2.27 (s, 3H).



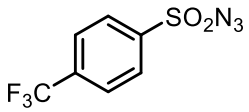
S6

1-azido-1,2-benziodoxol-3(1*H*)-one (S6): Prepared from **S5** according to the literature procedure.[24] A 20 mL vial was charged with a magnetic stir bar, **S5** (2.3 g, 7.5 mmol) and anhydrous methylene chloride (7.0 mL). 1.5 equivalents of azidotrimethylsilane (5.9 mL, 11 mmol) and 0.50 mol% trimethylsilyl trifluoromethanesulfonate (6.8 μL, 38 μmol) was added to the solution sequentially at room temperature (25 ℃). After 1 hour, the precipitate was filtered, washed with pentane (10 mL) twice and methylene chloride (10 mL) twice sequentially, and dried in vacuo to afford 1.8 g of **S6**. ^{1}H NMR spectrum of **S6** was matched with the literature.[24]

Isolated Yield: 83%

Physical Property: Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.35 – 8.29 (m, 1H), 8.04 – 7.95 (m, 2H), 7.79 (ddd, *J* = 7.5, 6.0, 2.1 Hz, 1H).



S7

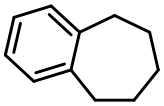
4-(trifluoromethyl)benzenesulfonyl azide (S7): Prepared according to the literature procedure.[17] A 100 mL round-bottom flask was charged with a magnetic stir bar, 4-(trifluoromethyl)benzene-1-sulfonyl chloride (122 mg, 5.00 mmol) and acetone (25 mL). A solution of 1.20 equivalents of sodium azide (390 mg, 6.00 mmol) in DI water (25 mL) was added dropwise at 0 ℃. The reaction was slowly warmed up to room temperature (25 ℃) and stirred for 5 hours. Acetone was evaporated *in vacuo* at room temperature (25 ℃) and extracted with methylene chloride three times. The resulting solution was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified through a short silica gel plug with methylene chloride to afford 119 mg of **S7**. ^{1}H and ^{19}F NMR spectrum of **S7** was matched with the literature.[38]

Isolated Yield: 95%

Physical Property: White solid.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.11 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ -63.4.



3n

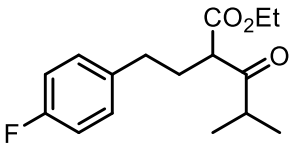
6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (3n): Prepared according to the literature procedure.[39] A 20 mL vial was charged with a magnetic stir bar, 6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (1.00 g, 6.16 mmol) and trifluoroacetic acid (10 mL). 1.50 equivalents of triethylsilane (1.48 mL, 9.24 mmol) was added to the solution at room temperature (25 ℃) and the solution was heated to 60 ℃. After 24 hours, the resulting mixture was cooled down to room temperature (25 ℃) and concentrated *in vacuo*. The crude solution was treated with cold water (100 mL) and extracted with ethyl acetate (100 mL) three times. The organic layer was washed with brine solution (100 mL), dried over MgSO4, filtered, and concentrated. The crude mixture was purified by flash chromatography (straight pentane) to afford 620 mg of **3n**. ^{1}H NMR spectrum of **3n** was matched with the literature.[40]

Isolated Yield: 69%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.09 (s, 4H), 2.85 – 2.73 (m, 4H), 1.84 (p, J = 5.9 Hz, 2H), 1.64 (p, J = 5.4 Hz, 4H).

Note: Overlapped fraction between **3n** and triethylsilane was collected and re-purified by flash column chromatography (pentane).



3t

ethyl 2-(4-fluorophenethyl)-4-methyl-3-oxopentanoate (3t): A 100 mL round-bottom flask was charged with a magnetic stir bar, 3.0 equivalents of dry NaH (90%; 1.6 g, 60 mmol) and anhydrous THF (10 mL). To the suspension of NaH was added a solution of 1.0 equivalents of ethyl isobutyrylacetate (3.2 mL, 20 mmol) in anhydrous THF (10 mL) dropwise at 0 ℃ at under a nitrogen atmosphere. The solution was warmed to room temperature (25 ℃) and stirred for 30 minutes. To the resulting mixture was added a solution of 1.5 equivalents of 4-fluorobenzyl bromide (3.7 mL, 30 mmol) in THF (10 mL) dropwise and stirred for 24 hours under reflux. The reaction mixture was cooled to 0 ℃, quenched with water (10 mL), and extracted with ethyl acetate (50 mL) three times. The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography (methylene chloride:pentane = 1:1 to 2:1) to afford 4.06 g of **3t**.

Isolated Yield: 72%

Physical Property: Colorless oil.

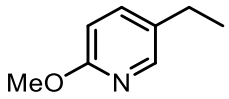
^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.15 – 7.10 (m, 2H), 7.00 – 6.94 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.59 (t, *J* = 7.1 Hz, 1H), 2.77 (hept, *J* = 6.9 Hz, 1H), 2.65 – 2.50 (m, 2H), 2.20 – 2.06 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 2H), 1.10 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ -117.2.

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 208.8, 169.6, 161.4 (d, *J* = 244.0 Hz), 136.5 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 7.8 Hz), 115.2 (d, *J* = 21.2 Hz), 61.4, 56.1, 40.5, 32.7, 29.8 (d, *J* = 1.1 Hz), 18.5, 18.1, 14.1.

IR (neat): 2973, 2935, 2874, 1739, 1711, 1509, 1219, 1155, 831 cm^{-1}.

HRMS (ESI) calculated for $C_{16}H_{22}FO_3^+$ $[M+H]^+$ 281.1547, found 281.1544.



3v

5-ethyl-2-methoxypyridine (3v): A 250 mL round-bottom flask was charged with a magnetic stir bar, 5-bromo-2-methoxypyridine (1.0 mL, 8.0 mmol) and anhydrous THF (16 mL). To the diluted solution was added a solution of 2.3 equivalents of 1.7 M *tert*-butyllithium (11 mL, 18 mmol) in THF dropwise at -78 ℃ at under a nitrogen atmosphere. After stirring for 1 hour, 10 equivalents of iodoethane (6.4 mL, 80 mmol) in 80 mL was added dropwise to the solution followed by stirring for additional 3 hours at -78 ℃. The solution was warmed up to 25 ℃, stirred for 5 hours, quenched with 20 mL of water and extracted with 20 mL of diethyl ether twice. The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography (diethyl ether:pentane = 1:3) to afford 0.6 g of **3v**.

Isolated Yield: 55%

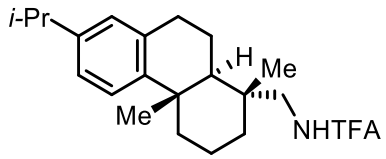
Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.98 (d, *J* = 2.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 162.7, 145.6, 138.6, 132.1, 110.5, 53.4, 25.3, 15.8.

IR (neat): 2963, 2873, 2361, 1606, 1492, 1286, 1026 cm^{-1}.

HRMS (ESI) calculated for $C_8H_{12}NO^+$ $[M+H]^+$ 138.0913, found 138.0913.



3ae

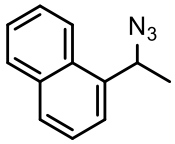
2,2,2-trifluoro-*N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)acetamide (3ae): Prepared adopting the literature procedure.[41] A 100 mL round-bottom flask was charged with a magnetic stir bar, ((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanamine (90% purity, 6.23 mmol, 1.98 g) and tetrahydrofuran (30 mL). 2.00 equivalents of triethylamine (12.5 mmol, 1.70 mL) and 1.10 equivalents of ethyl trifluoroacetate (6.85 mmol, 0.800 mL) was added to the solution sequentially at 0 ℃. The reaction mixture was heated under reflux. After 4 hours, the resulting solution was quenched with 1.0 M HCl (aq, 50 mL), washed with water and dried over Na_2SO_4. After evaporation of solvent, the crude mixture was purified by flash column chromatography (ethayl acetate:pentane = 1:8 to 1:4) to afford 1.52 g of **3ae**. ^{1}H NMR spectrum of **3ae** was matched with the literature.[42]

Isolated Yield: 64%

Physical Property: Amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.17 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.90 (s, 1H), 6.20 (s, 1H), 3.34 – 3.22 (m, 2H), 2.99 – 2.73 (m, 3H), 2.36 – 2.25 (m, 1H), 1.91 – 1.62 (m, 4H), 1.52 – 1.33 (m, 3H), 1.29 – 1.22 (m, 10H), 0.98 (s, 3H).

Note: Due to the hygroscopic nature of **3ae**, it should be dried in a vacuum desiccator for 24 hours and stored in a glovebox for the next step.



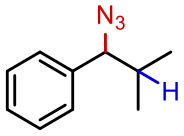
4a

1-(1-azidoethyl)naphthalene (4a): Prepared from 1-ethylnaphthalene (**3a**) according to Procedure B. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 73.2 mg of **4a**. ^{1}H NMR spectrum of **4a** was matched with the literature.[18]

Isolated Yield: 93%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.63 – 7.49 (m, 4H), 5.38 (q, J = 6.8 Hz, 1H), 1.75 (d, J = 6.8 Hz, 3H).



4b

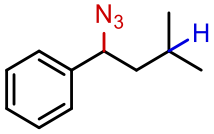
(1-azido-2-methylpropyl)benzene (4b): Prepared from isobutylbenzene (**3b**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:50) to afford 28.3 mg of **4b**. Regioselectivity of benzylic (**4b**)[13] and tertiary product[15] was determined by ^{1}H NMR analysis of crude mixture.

Yield and Site-Selectivity (^{1}H NMR): 44%, benzylic to tertiary product = 11:1.

Isolated Yield: 40% for only benzylic product (**4b**).

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 7.28 – 7.24 (m, 2H), 4.13 (d, J = 8.0 Hz, 1H), 1.98 (dh, J = 8.0, 6.7 Hz, 1H), 1.02 (d, J = 6.7 Hz, 3H), 0.79 (d, J = 6.7 Hz, 3H).



4c

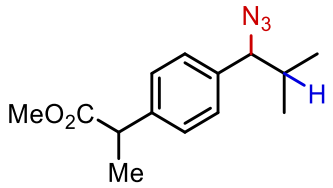
(1-azido-3-methylbutyl)benzene (4c): Prepared from isopentylbenzene (**3c**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:50) to afford 49.1 mg of **4c**. Regioselectivity of benzylic (**4c**)[14] and tertiary product[16] was determined by ^{1}H NMR analysis of crude mixture.

Yield and Site-Selectivity (^{1}H NMR): 71%, benzylic to tertiary product = 25:1.

Isolated Yield: 65% for only benzylic product (**4c**).

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.38 (tt, J = 7.0, 1.1 Hz, 2H), 7.35 – 7.28 (m, 3H), 4.46 (dd, J = 8.6, 6.4 Hz, 1H), 1.76 (ddd, J = 13.4, 8.6, 6.1 Hz, 1H), 1.65 (dp, J = 12.9, 6.4 Hz, 1H), 1.57 (ddd, J = 13.7, 7.3, 6.4 Hz, 1H), 0.94 (d, J = 6.4 Hz, 6H).



4d

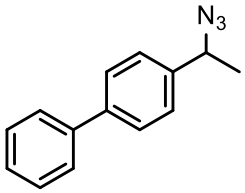
methyl 2-(4-(1-azido-2-methylpropyl)phenyl)propanoate (4d): Prepared from ibuprofen methyl ester (**3c**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:25) to afford 61.8 mg of **4d**. Regioselectivity of benzylic (**4d**)[18] and tertiary product was determined by ^{1}H NMR analysis of crude mixture.

Yield and Site-Selectivity (^{1}H NMR): 62%, benzylic to tertiary product = 30:1.

Isolated Yield: 59%, for only benzylic product (**4d**).

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 4.12 (d, J = 7.9 Hz, 1H), 3.73 (q, J = 7.2 Hz, 1H), 3.67 (s, 3H), 1.97 (dp, J = 7.9, 6.6 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H).



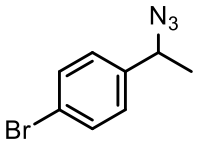
4e

4-(1-azidoethyl)-1,1'-biphenyl (4e): Prepared from 4-ethyl-1,1'-biphenyl (**3e**) according to Procedure B. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:40) to afford 40.5 mg of **4e**. ^{1}H NMR spectrum of **4e** was matched with the literature.[43]

Isolated Yield: 45%

Physical Property: White solid.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.63 – 7.55 (m, 4H), 7.44 (dd, J = 8.4, 6.9 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 4.66 (q, J = 6.8 Hz, 1H), 1.56 (d, J = 6.8 Hz, 3H).



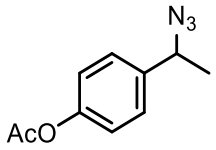
4f

1-(1-azidoethyl)-4-bromobenzene (4f): Prepared from 1-bromo-4-ethylbenzene (**3f**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:40) to afford 55.0 mg of **4f**. ^{1}H NMR spectrum of **4f** was matched with the literature.[44]

Isolated Yield: 61%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.53 – 7.47 (m, 2H), 7.23 – 7.17 (m, 2H), 4.59 (q, J = 6.8 Hz, 1H), 1.51 (d, J = 6.8 Hz, 3H).



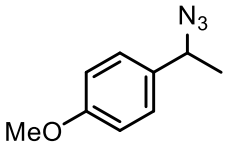
4g

4-(1-azidoethyl)phenyl acetate (4g): Prepared from 4-ethylphenyl acetate (**3g**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:15) to afford 46.0 mg of **4g**. ^{1}H NMR spectrum of **4g** was matched with the literature.[18]

Isolated Yield: 56%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.37 – 7.31 (m, 2H), 7.13 – 7.07 (m, 2H), 4.62 (q, *J* = 6.8 Hz, 1H), 2.30 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H).



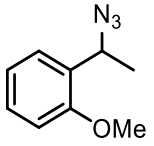
4h

1-(1-azidoethyl)-4-methoxybenzene (4h): Prepared from 1-ethyl-4-methoxybenzene (**3h**) according to Procedure D. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:12) to afford 28.7 mg of **4h**. ^{1}H NMR spectrum of **4h** was matched with the literature.[44]

Isolated Yield: 81%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.29 – 7.23 (m, 2H), 6.94 – 6.88 (m, 2H), 4.57 (q, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H).



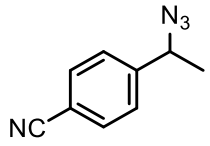
4i

1-(1-azidoethyl)-2-methoxybenzene (4i): Prepared from 1-ethyl-2-methoxybenzene (**3i**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:12) to afford 40.5 mg of **4i**. ^{1}H NMR spectrum of **4i** was matched with the literature.[45]

Isolated Yield: 57%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.35 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.06 (q, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H).



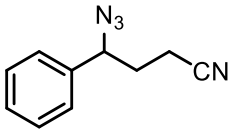
4j

4-(1-azidoethyl)benzonitrile (4j): Prepared from 4-ethylbenzonitrile (**3j**) according to Procedure B. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:25) to afford 17.4 mg of **4j**. ^{1}H NMR spectrum of **4j** was matched with the literature.[13]

Isolated Yield: 25%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.74 – 7.62 (m, 2H), 7.49 – 7.40 (m, 2H), 4.69 (q, J = 6.8 Hz, 1H), 1.55 (d, J = 6.9 Hz, 3H).



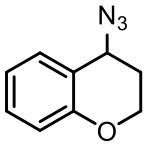
4k

4-azido-4-phenylbutanenitrile (4k): Prepared from 4-phenylbutanenitrile (**3k**) according to Procedure B. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 38.0 mg of **4k**. ^{1}H NMR spectrum of **4k** was matched with the literature.[46]

Isolated Yield: 51%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.45 – 7.40 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.31 (m, 2H), 4.63 (dd, J = 8.7, 5.7 Hz, 1H), 2.53 – 2.33 (m, 2H), 2.15 – 1.98 (m, 2H).



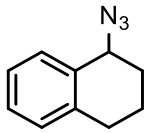
4l

4-azidochroman (4l): Prepared from chroman (**3l**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 42.2 mg of **4l**. ^{1}H NMR spectrum of **4l** was matched with the literature.[13]

Isolated Yield: 60%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.28 – 7.19 (m, 2H), 6.95 (td, J = 7.4, 1.2 Hz, 1H), 6.91 – 6.85 (m, 1H), 4.60 (t, J = 4.0 Hz, 1H), 4.29 (dtd, J = 11.3, 4.0, 1.1 Hz, 1H), 4.22 (td, J = 11.2, 2.5 Hz, 1H), 2.18 (ddt, J = 14.2, 11.1, 4.3 Hz, 1H), 2.03 (dtd, J = 14.2, 3.7, 2.5 Hz, 1H).



4m

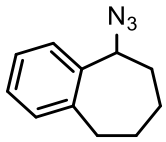
1-azido-1,2,3,4-tetrahydronaphthalene (4m): Prepared from 1,2,3,4-tetrahydronaphthalene (**3m**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 62.6 mg of **4m**. ^{1}H NMR spectrum of **4m** was matched with the literature.[13]

Isolated Yield: 90%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS)

δ 7.32 – 7.28 (m, 1H), 7.26 – 7.19 (m, 2H), 7.14 (dd, *J* = 7.1, 1.8 Hz, 1H), 4.57 (t, *J* = 4.5 Hz, 1H), 2.85 (dt, *J* = 16.3, 5.0 Hz, 1H), 2.75 (dt, *J* = 17.2, 7.1 Hz, 1H), 2.06 – 1.93 (m, 3H), 1.88 – 1.77 (m, 1H).



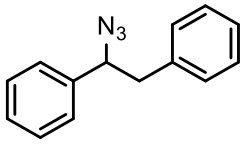
4n

5-azido-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (4n): Prepared from 6,7,8,9-tetrahydro-5H-benzo[7]annulene (**3n**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 63.8 mg of **4n**. ^{1}H NMR spectrum of **4n** was matched with the literature.[13]

Isolated Yield: 85%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.30 – 7.26 (m, 1H), 7.22 – 7.16 (m, 2H), 7.15 – 7.12 (m, 1H), 4.80 – 4.75 (m, 1H), 3.00 (ddd, *J* = 14.5, 9.9, 2.0 Hz, 1H), 2.72 (ddd, *J* = 14.4, 8.6, 1.8 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.98 – 1.86 (m, 2H), 1.81 (dtt, *J* = 14.0, 7.2, 3.5 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.65 – 1.55 (m, 1H).



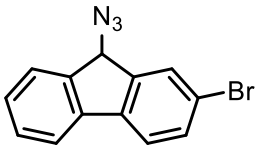
4o

(1-azidoethane-1,2-diyl)dibenzene (4o): Prepared from 1,2-diphenylethane (**3o**) according to Procedure D. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:40) to afford 32.1 mg of **4o**. ^{1}H NMR spectrum of **4o** was matched with the literature.[18]

Isolated Yield: 72%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.39 – 7.30 (m, 3H), 7.29 – 7.20 (m, 5H), 7.17 – 7.11 (m, 2H), 4.66 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.12 – 2.98 (m, 2H).



4p

9-azido-2-bromo-9*H*-fluorene (4p): Prepared from 2-bromo-9H-fluorene (**3p**) according to Procedure D. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:20) to afford 27.6 mg of **4p**.

Isolated Yield: 48%

Physical Property: White solid.

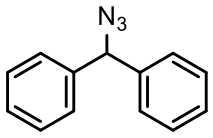
Melting Point: 82-84 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.76 (q, *J* = 1.1 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.63 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.57 (d, *J* = 1.1 Hz, 2H), 7.48 – 7.43 (m, 0H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 5.18 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 143.7, 141.3, 139.7, 139.7, 132.6, 129.7, 128.6, 128.4, 125.3, 121.64, 121.57, 120.4, 63.9.

IR (neat): 2925, 2092, 1447, 765, 741, 427 cm^{-1}.

HRMS (ESI) calculated for $C_{13}H_8BrN_3^+$ $[M]^+$ 284.9896, found 284.9890.



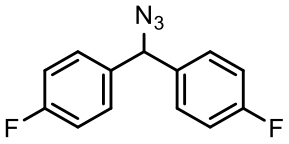
4q

(azidomethylene)dibenzene (4q): According to Procedure A in 10 mmol scale, a 250 mL round-bottom flask was charged with diphenylmethane (**3q**, 1.68 g, 10.0 mmol), 2.00 mol% of copper(II) acetate (36 mg, 0.2 mmol), 4.0 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (128 mg, 0.400 mmol), 2.50 equivalents of *N*-fluorobenzenesulfonimide (7.88 g, 25.0 mmol), and a magnetic stir bar outside a glovebox. The flask was capped with serrated natural rubber septum. The septum was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the flask was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the flask was taken out of the glovebox and equipped with a balloon filled with nitrogen gas. The flask was charged with nitromethane (50 mL, 0.2 M) and 3.60 equivalents of azidotrimethylsilane (4.78 mL, 1.44 mmol) sequentially, stirred, and heated to 30 ℃ (inner temperature) in a heating block on a hot plate. After 24 hours, the flask was cooled to room temperature (25 ℃), charged with 3.00 equivalents of lithium(I) carbonate (2.21 g, 30.0 mmol), stirred for 30 minutes, and stayed in air for 30 minutes. All precipitates and catalysts were filtered out through a silica plug (glass Buchner funnel with frit) with dichloromethane (50 mL x 3 times). After evaporation of solvent on a rotary evaporator at 30 ℃, flash column chromatography (ethyl acetate:pentane = 1:30) was performed. The isolated compound was dried to give 1.7 g of **4q**. ^{1}H NMR spectrum of **4q** was matched with the literature.[47]

Isolated Yield: 81%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.40 – 7.27 (m, 10H), 5.71 (s, 1H).



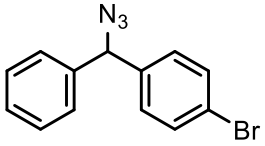
4r

4,4'-(azidomethylene)bis(fluorobenzene) (4r): Prepared from bis(4-fluorophenyl)methane (**3r**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 58.5 mg of **4r**. ^{1}H NMR spectrum of **4r** was matched with the literature.[47]

Isolated Yield: 60%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.29 – 7.23 (m, 4H), 7.09 – 7.02 (m, 4H), 5.68 (s, 1H).



4s

1-(azido(phenyl)methyl)-4-bromobenzene (4s): Prepared from 1-benzyl-4-bromobenzene (**3s**) according to Procedure D. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 29.2 mg of **4s**.

Isolated Yield: 51%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS)

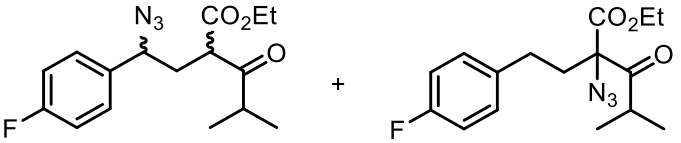
δ 7.51 – 7.45 (m, 2H), 7.39 – 7.26 (m, 5H), 7.22 – 7.16 (m, 2H), 5.66 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS)

δ 139.0, 138.7, 131.8, 129.0, 128.8, 128.3, 127.4, 122.0, 67.9.

IR (neat): 3029, 2096, 1486, 1239, 1071, 1010, 698, 480 cm^{-1}.

HRMS (ESI) calculated for $C_{13}H_{10}Br^{+}$ $[M\text{-}N_3]^{+}$ 244.9960, found 244.9962.



4t **4u**

ethyl 2-(2-azido-2-(4-fluorophenyl)ethyl)-4-methyl-3-oxopentanoate (4t) and **ethyl 2-azido-2-(4-fluorophenethyl)-4-methyl-3-oxopentanoate (4u)**: Prepared from ethyl 2-(4-fluorophenethyl)-4-methyl-3-oxopentanoate (**3t**) according to Procedure E. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:30) to afford 16.8 mg of **4t** (d.r. = 1.1:1.0) along with 16.5 mg of the regioisomer **4u**. ^{1}H NMR spectrum of **4t** was matched with the literature.[48]

ethyl 2-(2-azido-2-(4-fluorophenyl)ethyl)-4-methyl-3-oxopentanoate (4t):

Isolated Yield: 26%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) for inseparable diastereomers; d.r = 1.1:1.0 based on ^{1}H NMR analysis of the crude reaction mixture. A and B represents each diastereomer. δ 7.33 – 7.27 (m, 4H, A and B), 7.13 – 7.03 (m, 4H, A and B), 4.53 (dd, *J* = 9.8, 5.0 Hz, 1H, CHN_3 of A), 4.40 (dd, *J* = 9.7, 5.2 Hz, 1H, CHN_3 of B), 4.25 – 4.15 (m, 4H, A and B), 3.86 – 3.77 (m, 2H, A and B), 2.89 – 2.75 (m, 2H, A and B), 2.31 – 2.08 (m, 4H, A and B), 1.32 – 1.24 (m, 6H, A and B), 1.16 – 1.06 (m, 12H, A and B).

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) for **4t-A**; ^{1}H NMR spectrum includes 13% of **4t-B** (diasteomer) but the peaks of **4t-B** was distinguished and ignored for characterization of a single diastereomer **4t-A**). δ 7.33 – 7.27 (m, 2H), 7.13 – 7.03 (m, 2H), 4.53 (dd, *J* = 9.8, 5.0 Hz, 1H), 4.20 (qd, *J* = 7.2, 1.3 Hz, 2H), 2H), 3.82 (dd, *J* = 8.6, 5.3 Hz, 1H), 2.82 (dq, *J* = 13.8, 7.0 Hz, 1H), 2.25 (ddd, *J* = 13.8, 8.6, 5.0 Hz, 1H), 2.14 (ddd, *J* = 14.5, 9.7, 5.3 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 3H).

ethyl 2-azido-2-(4-fluorophenethyl)-4-methyl-3-oxopentanoate (4u):

Isolated Yield: 26%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.17 – 7.12 (m, 2H), 7.00 – 6.94 (m, 2H), 4.34 – 4.22 (m, 2H), 3.04 (hept, *J* = 6.7 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.32 – 2.19 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 161.5 (d, *J* = 244.2 Hz), 136.1 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 7.9 Hz), 115.3 (d, *J* = 21.2 Hz), 35.2 (d, *J* = 1.2 Hz).

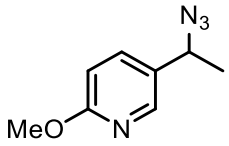
^{19}F NMR (377 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ – 116.86.

DEPT-135 NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS)

δ 129.8 (d, *J* = 7.9 Hz, positive), 115.3 (d, *J* = 21.2 Hz, positive), 62.9 (negative), 36.4 (positive), 35.2 (negative), 29.5 (negative), 19.6 (positive), 19.4 (positive), 14.1 (positive).

IR (neat): 2977, 2937, 2875, 2111, 1723, 1509, 1221, 1014, 829 cm^{-1}.

HRMS (ESI) calculated for $C_{16}H_{21}FN_3O_3^+$ $[M+H]^+$ 322.1561, found 322.1560.



4v

5-(1-azidoethyl)-2-methoxypyridine (4v): Prepared from 5-ethyl-2-methoxypyridine (**3v**) according to Procedure A in 0.2 mmol scale. The reaction mixture was purified by flash column chromatography (diethyl ether:pentane = 1:3) to afford 10.8 mg of **4v**.

Isolated Yield: 30%

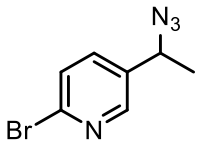
Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.11 (d, *J* = 2.5 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 1H), 3.94 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 164.3, 145.2, 136.9, 129.2, 111.4, 58.5, 53.7, 21.4.

IR (neat): 2976, 2941, 2098, 1604, 1491, 1316, 1281, 1020 cm^{-1}.

HRMS (ESI) calculated for $C_8H_{11}N_4O^+$ $[M]^+$ 179.0927, found 179.0926.



4w

5-(1-azidoethyl)-2-bromopyridine (4w): Prepared from 2-bromo-5-ethylpyridine (**3w**) according to Procedure B in 0.2 mmol scale. The reaction mixture was purified by flash column chromatography (diethyl ether:pentane = 1:3) to afford 13.8 mg of **4w**.

Isolated Yield: 30%

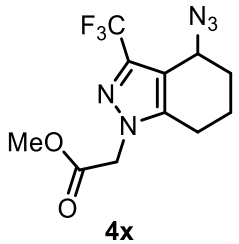
Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.34 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.48 (m, 2H), 4.66 (q, *J* = 6.8 Hz, 1H), 1.56 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 148.5, 141.9, 136.6, 136.1, 128.4, 58.1, 21.6.

IR (neat): 2978, 2925, 2101, 1572, 1454, 1248, 1090 cm^{-1}.

HRMS (ESI) calculated for $C_7H_8BrN_4^+$ $[M]^+$ 226.9927, found 226.9924.



4x

methyl 2-(4-azido-3-(trifluoromethyl)-4,5,6,7-tetrahydro-1*H*-indazol-1-yl)acetate (4x): Prepared from methyl 2-(3-(trifluoromethyl)-4,5,6,7-tetrahydro-1*H*-indazol-1-yl)acetate (**3x**) according to Procedure D in 0.2 mmol scale. The reaction mixture was purified by flash column chromatography (diethyl ether:pentane = 1:1) to afford 39.6 mg of **4x**.

Isolated Yield: 65%

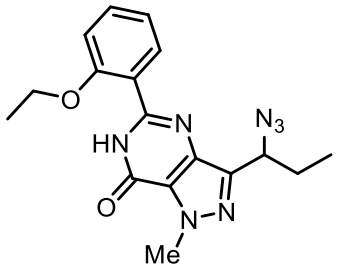
Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 4.91 (d, *J* = 17.6 Hz, 1H), 4.81 (d, *J* = 17.6 Hz, 1H), 4.72 – 4.66 (m, 1H), 3.78 (s, 3H), 2.65 (ddd, *J* = 16.5, 5.4, 3.4 Hz, 1H), 2.51 (ddd, *J* = 16.5, 10.0, 7.0 Hz, 1H), 2.14 – 2.05 (m, 1H), 2.03 – 1.91 (m, 2H), 1.84 (ddt, *J* = 13.8, 11.3, 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 167.2, 143.1, 140.1 (q, J = 37.6 Hz), 121.4 (q, J = 269.5 Hz), 113.4, 53.0, 52.0, 50.9, 29.3, 21.0, 17.6.

IR (neat): 2954, 2861, 2098, 1755, 1213, 1127 cm^{-1}.

HRMS (ESI) calculated for $C_{11}H_{13}F_3N_5O_2^+$ $[M+H]^+$ 304.1016, found 304.1011.



4y

3-(1-azidopropyl)-5-(2-ethoxyphenyl)-1-methyl-1*H*-pyrazolo[4,3-*d*]pyrimidin-7(6*H*)-one (4y): Prepared from 5-(2-ethoxyphenyl)-1-methyl-3-propyl-1*H*-pyrazolo[4,3-d]pyrimidin-7(6*H*)-one (**3y**) according to Procedure D. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 2:1) to afford 21.5 mg of **4y**.

Isolated Yield: 30%

Physical Property: White solid.

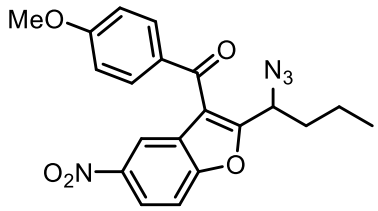
Melting Point: 111-113 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 11.26 (s, 1H), 8.50 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.47 (ddd, *J* = 8.8, 7.4, 1.9 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.05 (dd, *J* = 8.4, 0.9 Hz, 1H), 4.77 (t, *J* = 7.4 Hz, 1H), 4.34 – 4.28 (m, 5H), 2.23 (p, *J* = 7.4 Hz, 2H), 1.62 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 156.6, 153.6, 149.4, 143.5, 138.5, 132.7, 131.3, 125.0, 121.9, 119.7, 112.9, 65.4, 59.6, 38.7, 26.6, 14.7, 11.0.

IR (neat): 3296, 2975, 2935, 2095, 1696, 1588, 1484, 1234, 1033, 763 cm^{-1}.

HRMS (ESI) calculated for $C_{17}H_{20}N_7O_2^+$ $[M+H]^+$ 354.1673, found 354.1671.



4z

(2-(1-azidobutyl)-5-nitrobenzofuran-3-yl)(4-methoxyphenyl)methanone (4z): Prepared from (2-butyl-5-nitrobenzofuran-3-yl)(4-methoxyphenyl)methanone (**3z**) according to Procedure B. The reaction mixture was purified by flash column chromatography (methylene chloride:pentane = 2:3) to afford 86.5 mg of **4z**.

Isolated Yield: 55%

Physical Property: White solid.

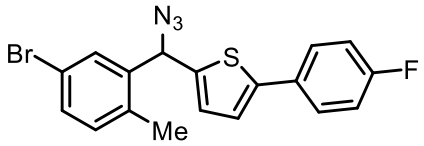
Melting Point: 64-66 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.36 – 8.27 (m, 2H), 7.90 – 7.84 (m, 2H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.05 – 6.99 (m, 2H), 4.80 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 2.11 – 1.96 (m, 2H), 1.53 – 1.42 (m, 1H), 1.40 – 1.28 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 187.8, 164.5, 161.6, 156.5, 144.9, 132.0, 130.3, 126.8, 121.4, 119.4, 118.4, 114.3, 112.3, 56.8, 55.7, 34.5, 19.3, 13.5.

IR (neat): 3103, 2961, 2934, 2099, 1598, 1527, 1344, 1252, 1168, 900, 837 cm^{-1}.

HRMS (ESI) calculated for $C_{20}H_{19}N_4O_5^+$ $[M+H]^+$ 395.1350, found 395.1346.



4aa

2-(azido(5-bromo-2-methylphenyl)methyl)-5-(4-fluorophenyl)thiophene (4aa): Prepared from 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (**3aa**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:10) to afford 29.2 mg of **4aa**.

Isolated Yield: 36%

Physical Property: Yellow oil.

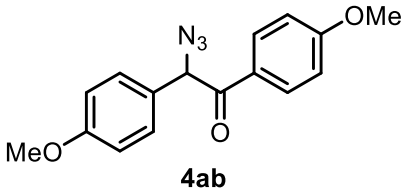
^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.70 (d, *J* = 2.1 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.39 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.09 (d, *J* = 3.7 Hz, 1H), 7.08 – 7.02 (m, 3H), 6.89 (dd, *J* = 3.7, 0.8 Hz, 1H), 5.99 (s, 1H), 2.23 (s, 3H).

^{19}F NMR (377 MHz, CDCl3 containing 1 % (v/v) TMS) δ -113.9.

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 162.5 (d, *J* = 247.9 Hz), 140.6, 139.1, 134.4, 132.4, 131.4, 130.1 (d, *J* = 3.4 Hz), 129.6, 127.7, 127.5 (d, *J* = 8.1 Hz), 122.64, 122.63, 120.1, 115.9 (d, *J* = 22.0 Hz), 61.1, 18.9.

IR (neat): 2922, 2852, 2097, 1546, 1233, 808 cm^{-1}.

HRMS (ESI) calculated for $C_{18}H_{13}BrFS^+$ $[M-N_3]^+$ 358.9900, found 358.9897.



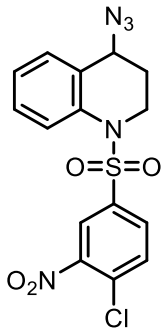
4ab

2-azido-1,2-bis(4-methoxyphenyl)ethanone (4ab): Prepared from 1,2-bis(4-methoxyphenyl)ethanone (**3ab**) according to Procedure A. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:8) to afford 72.9 mg of **4ab**. ^{1}H NMR spectrum of **4ab** was matched with the literature.[49]

Isolated Yield: 62%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.88 – 7.84 (m, 2H), 7.33 – 7.28 (m, 2H), 6.93 – 6.89 (m, 2H), 6.88 – 6.84 (m, 2H), 5.63 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H).



4ac

4-azido-1-((4-chloro-3-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (4ac): Prepared from 1-((4-chloro-3-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (**3ac**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:10) to afford 33.2 mg of **4ac**.

Isolated Yield: 42%

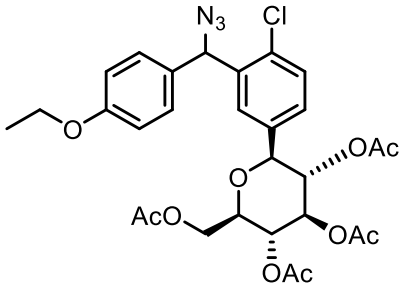
Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.13 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.67 (dd, J = 8.5, 2.1 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.40 (ddd, J = 8.6, 6.3, 2.7 Hz, 1H), 7.26 – 7.20 (m, 2H), 4.46 (t, J = 4.1 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.74 (ddd, J = 13.1, 11.4, 4.1 Hz, 1H), 1.98 (dq, J = 14.1, 4.1 Hz, 1H), 1.91 – 1.80 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 147.6, 138.4, 135.3, 132.9, 132.2, 130.8, 130.0, 129.6, 126.9, 125.7, 124.4, 124.0, 56.6, 42.9, 27.5.

IR (neat): 3092, 2929, 2097, 1537, 1349, 1174, 887, 762 cm^{-1}.

HRMS (ESI) calculated for $C_{15}H_{12}ClN_5NaO_4S^+$ $[M+Na]^+$ 416.0191, found 416.0188.



4ad

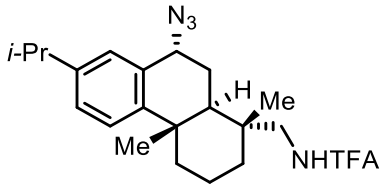
(2*R*,3*R*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-(3-(azido(4-ethoxyphenyl)methyl)-4-chlorophenyl)tetrahydr-o-2*H*-pyran-3,4,5-triyl triacetate (4ad): Prepared from dapagliflozin tetraacetate (**3ad**) according to Procedure C. The reaction mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:4) to afford an inseparable mixture of **3ad** and **4ad** (d.r. = 1.4:1.0).

Note: The yield of **3ad** and **4ad**, and the diastereomeric ratio of **4ad** were measured after filtration through a silica pad.

Yield (^{1}H NMR): 34%

Physical Property: White solid.

HRMS (ESI) calculated for $C_{29}H_{32}ClN_3NaO_{10}^+$ $[M+Na]^+$ 640.1668, found 640.1661.



(–)-**4ae**

***N*-(((1*R*,4a*S*,9*R*,10a*R*)-9-azido-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2,2,2-trifluoroacetamide ((–)-4ae)**: Prepared from **3ae** in 0.2 mmol scale according to Procedure A. The major diastereomer (47.0 mg of (–)-**4ae**) was separated from the minor diastereomer via flash column chromatography (ethyl acetate:pentane = 1:20). The relative configuration (d.r. = 6.0:1.0) was determined by ^{1}H, ^{13}C, DEPT-135, HSQC, HMBC, and TOCSY NMR analysis and then confirmed with the literature[50] after reduction of azide to primary amine group.

For 2.0 mmol reaction scale, a 50 mL round-bottom flask was charged with 2.00 mol% of copper(II) acetate (7.30 mg, 20.0 μmol), 4.0 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (25.6 mg, 40.0 μmol), 2.50 equivalents of *N*-fluorobenzenesulfonimide (1.58 g, 5.00 mmol), and a magnetic stir bar outside a glovebox. The flask was capped with serrated natural rubber septum. The septum was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the flask was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the flask was taken out of the glovebox and equipped with a balloon filled with nitrogen gas. The flask was charged with the solution of **3ae** (763 mg, 2.00 mmol) in 50 mL of nitromethane (0.20 M) and 3.60 equivalents of azidotrimethylsilane (956 μL, 7.20 mmol) sequentially, stirred, and heated to 30 ℃ (inner temperature) in an oil bath on a hot plate. After 24 hours, the flask was cooled to room temperature (25 ℃), charged with 3.00 equivalents of lithium(I) carbonate (222 mg, 6.00 mmol), stirred for 30 minutes, and stayed in air for 30 minutes. All precipitates and catalysts were filtered out through a silica plug (glass Buchner funnel with frit) with dichloromethane (10 mL x 3 times) and nitromethane (10 mL x 3 times). After evaporation of solvent on a rotary evaporator at 30 ℃, flash column chromatography (ethyl acetate:pentane = 1:20) was performed. The isolated compound was dried to give 450.0 mg of (–)-**4ae** (d.r. = 5.8:1.0).

Yield (^{1}H NMR): Total 63% for both diastereomers in 0.2 mmol scale and total 62% in 2.0 mmol scale.

Isolated Yield: 56% and 53% of (–)-**4ae** in 0.2 mmol scale and 2.0 mmol scale respectively.

Physical Property: Amorphous solid.

Melting Point: 122-124 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.30 – 7.19 (m, 2H), 6.99 (d, *J* = 1.9 Hz, 1H), 4.76 (dd, *J* = 3.7, 2.2 Hz, 1H), 3.54 (dd, *J* = 14.1, 9.9 Hz, 1H), 3.00 – 2.85 (m, 2H), 2.26 (dd, *J* = 13.1, 3.6 Hz, 1H), 1.94 (ddd, *J* = 13.8, 12.1, 3.7 Hz, 1H), 1.85 – 1.64 (m, 4H), 1.45 – 1.28 (m, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.21 (s, 3H), 0.95 (s, 3H).

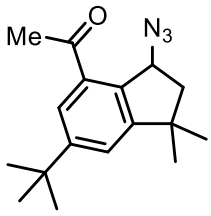
^{19}F NMR (377 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ -76.0.

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 157.9 (q, *J* = 36.7 Hz), 147.0, 146.7, 131.1, 127.8, 127.5, 126.0, 116.2 (q, *J* = 288.1 Hz), 61.9, 48.6, 40.3, 38.32, 38.29, 37.4, 35.3, 33.6, 25.6, 24.7, 24.1, 23.8, 19.4, 18.6.

DEPT-135 NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 127.8 (positive), 127.5 (positive), 126.0 (positive), 61.9 (positive), 48.6 (negative), 40.3 (positive), 38.3 (negative), 35.3 (negative), 33.6 (positive), 25.6 (negative), 24.7 (positive), 24.1 (positive), 23.8 (positive), 19.4 (positive), 18.6 (negative).

IR (neat): 3336, 2958, 2930, 2870, 2102, 1725, 1207, 1162, 830, 609 cm^{-1}.

HRMS (ESI) calculated for $C_{22}H_{29}F_3N_4NaO$+ $[M+Na]^+$ 445.2186, found 445.2183.
$[\alpha]_D^{24}$ = -20º (c = 0.40, $CHCl_3$)



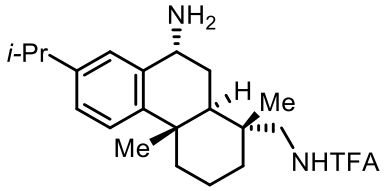
4af

1-(3-azido-6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethanone (4af): According to Procedure A, a 100 mL round-bottom flask was charged with celestolide (**3af**, 1.22 g, 5.00 mmol) 2.00 mol% of copper(II) acetate (18.0 mg, 0.100 mmol), 4.00 mol% of 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] (64.0 mg, 0.200 mmol), 2.50 equivalents of *N*-fluorobenzenesulfonimide (3.94 g, 12.5 mmol), and a magnetic stir bar outside a glovebox. The flask was capped with serrated natural rubber septum. The septum was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the flask was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the flask was taken out of the glovebox and equipped with a balloon filled with nitrogen gas. The flask was charged with nitromethane (25 mL, 0.2 M) and 3.60 equivalents of azidotrimethylsilane (2.40 mL, 18.0 mmol) sequentially, stirred, and heated to 30 °C (inner temperature) in an oil bath on a hot plate. After 24 hours, the flask was cooled to room temperature (25 °C), charged with 3.00 equivalents of lithium(I) carbonate (1.10 g, 15.0 mmol), stirred for 30 minutes, and stayed in air for 30 minutes. All precipitates and catalysts were filtered out through a silica plug (glass Buchner funnel with frit) with dichloromethane (25 mL x 3 times). After evaporation of solvent on a rotary evaporator at 30 °C, flash column chromatography (ethyl acetate:pentane = 1:40) was performed. The isolated compound was dried to give 1.25 g of **4af**. ^{1}H NMR spectrum of **4af** was matched with the literature.[18]

Isolated Yield: 92%

Physical Property: Yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 5.59 (dd, *J* = 7.4, 1.8 Hz, 1H), 2.65 (s, 3H), 2.19 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.08 (dd, *J* = 13.7, 1.8 Hz, 1H), 1.38 (s, 9H), 1.34 (s, 3H), 1.32 (s, 3H).



5

***N*-(((1*R*,4a*S*,9*R*,10a*R*)-9-amino-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthre-n-1-yl)methyl)-2,2,2-trifluoroacetamide ((–)-5)**:

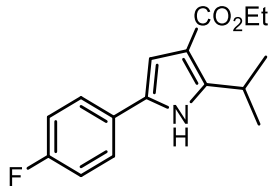
For 69 μmol scale, a 4 mL vial was charged with a magnetic stir bar, 2.0 equivalents of resin-bound triphenylphosphine (3 mmol/g grade, 23 mg, 0.14 mmol) and the resin was washed with THF (1.0 mL) three times and dried *in vacuo*. (–)-**4ae** (69 μmol, 23 mg), 0.1 M THF (0.7 mL), and 0.1 M DI water (0.7 mL) were added to the vial at room temperature (25 °C). After vigorous stirring for 6 hours, the solution was filtered, concentrated, and purified by flash column chromatography (methanol:methylene chloride = 1:19) to afford 25.0 mg of (–)-**5**. ^{1}H NMR spectrum of (–)-**5** was matched with the literature.[50]

For 0.2 mmol scale, a 20 mL borosilicate glass vial was charged with 2.00 equivalents of resin-bound triphenylphosphine (3 mmol/g grade, 133 mg, 0.400 mmol) and the resin was washed with THF (3.0 mL) three times and dried *in vacuo*. (–)-**4ae** (0.200 mmol, 76.0 mg), 0.1 M THF (2 mL), and 0.1 M DI water (2 mL) were added to the vial at room temperature (25 °C). After vigorous stirring for 9 hours, the solution was filtered, concentrated, and purified by flash column chromatography (methanol:methylene chloride = 1:19) to afford 84.7 mg of (–)-**5**.

Isolated Yield: 91% for 69 μmol scale, 85% for 0.2 mmol scale.

Physical Property: Hygroscopic pale-yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.68 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 4.24 (dd, *J* = 3.8, 2.0 Hz, 1H), 3.57 (dd, *J* = 13.9, 8.6 Hz, 1H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.87 (hept, *J* = 6.9 Hz, 1H), 2.73 – 2.08 (m, 3H), 1.99 (d, *J* = 11.9 Hz, 1H), 1.87 – 1.72 (m, 2H), 1.65 (dp, *J* = 14.2, 3.6 Hz, 1H), 1.58 (d, *J* = 12.8 Hz, 1H), 1.43 – 1.36 (m, 1H), 1.31 (ddd, *J* = 13.3, 6.1, 4.1 Hz, 2H), 1.24 (dd, *J* = 6.9, 1.2 Hz, 6H), 1.22 (s, 3H), 0.96 (s, 3H).



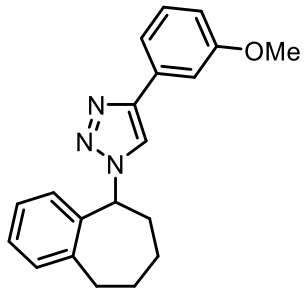
6

ethyl 5-(4-fluorophenyl)-2-isopropyl-1*H*-pyrrole-3-carboxylate (6): Prepared modifying to the literature procedure.[48] A 4 mL borosilicate glass vial was charged with a magnetic stir bar, 10.0 μmol of **4t** (3.20 mg), 12.5 μM of anhydrous THF (800 μL), 3.0 equivalents of triphenylphosphine (7.9 mg, 30 μmol) sequentially and stirred under N_2 gas for 24 hours at room temperature (25 ℃). After the removal of solvent, 10 wt% Pd/C (1.40 mg) and 300 μL of *o*-xylene was added to the vial. The resulting mixture was sonicated for 30 minutes and stirred at 145 °C for 10 hours. The solution was filtered through a silica plug, concentrated, and purified by flash column chromatography (diethyl ether:pentane = 1:2) to afford **6**. After purification, the exact yield (1.65 mg) was determined by ^{1}H NMR analysis with mesitylene as an external standard. ^{1}H NMR spectrum of **6** was matched with the literature.[48]

Isolated Yield: 60%

Physical Property: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 8.28 (bs, 1H), 7.47-7.37 (m, 2H), 7.12-7.05 (m, 2H), 6.77 (d, *J* = 2.9 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.86 (sept, *J* = 7.1 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 (d, *J* = 7.1 Hz, 6H).



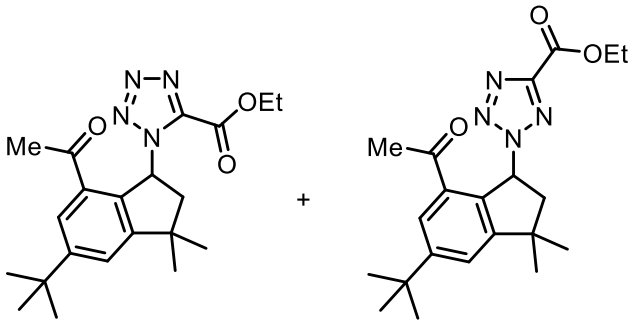
7

4-(3-methoxyphenyl)-1-(6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)-1*H*-1,2,3-triazole (7): Prepared modifying to the literature procedure.[51] A 4 mL borosilicate glass vial was charged with a magnetic stir bar, **4n** (0.120 mmol, 22.5 mg), 1.10 equivalents of 1-ethynyl-3-methoxybenzene (0.132 mmol, 17.0 μL), and 0.4 M THF (0.3 mL). To the solution was added 20.0 mol% $CuSO_4 \cdot 5H2O$ (24.0 μmol, 50.0 mg), 20.0 mol% sodium ascorbate (24.0 μmol, 4.80 mg), and 0.4 M DI water (0.3 mL) sequentially at room temperature (25 ℃). After vigorous stirring under nitrogen gas for 12 hours, 10 mL of water was added to the reaction mixture and organic layer was separated from extraction with ethyl acetate (20 mL) three times. The crude mixture was purified by flash column chromatography (ethyl acetate:pentane = 1:8) to afford 32.7 mg of **7**. ^{1}H NMR spectrum of **7** was matched with the literature.[51]

Isolated Yield: 85%

Physical Property: White solid.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.70 (s, 1H), 7.49 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.38 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.09 (td, *J* = 7.2, 2.2 Hz, 1H), 6.89 (ddd, *J* = 8.2, 2.6, 1.1 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 9.5 Hz, 1H), 3.87 (s, 3H), 2.85 (dddd, *J* = 42.9, 14.8, 9.2, 1.9 Hz, 2H), 2.60 – 2.47 (m, 1H), 2.44 – 2.35 (m, 1H), 2.13 – 2.05 (m, 1H), 2.00 – 1.85 (m, 2H), 1.64 – 1.52 (m, 1H).



8 **9**

ethyl 1-(7-acetyl-5-(*tert*-butyl)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl)-1*H*-tetrazole-5-carboxylate (8) and **ethyl 2-(7-acetyl-5-(*tert*-butyl)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl)-2*H*-tetrazole-5-carboxylate (9)**: A 4 mL borosilicate glass vial was charged with a magnetic stir bar, **4af** (0.10 mmol, 27 mg), 13 equivalents of ethyl carbonocyanidate (1.3 mmol, 0.13 g), and 1.0 equivalents of $ZnBr_2$ (0.10 mmol 23 mg) at room temperature (25 ℃). After vigorous stirring for 45 hours, the crude mixture was directly purified flash column chromatography (ethyl acetate:pentane = 1:4) to afford 17.0 mg of **8** and 21.2 mg of **9**.

ethyl 1-(7-acetyl-5-(*tert*-butyl)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl)-1*H*-tetrazole-5-carboxylate (8):

Isolated Yield: 44%

Physical Property: White solid.

Melting Point: 117-119 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.79 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.12 (dd, *J* = 8.9, 4.3 Hz, 1H), 4.62 (qt, *J* = 7.1, 3.6 Hz, 2H), 2.75 (dd, *J* = 14.1, 8.9 Hz, 1H), 2.21 (dd, *J* = 14.1, 4.3 Hz, 1H), 1.54 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.40 (s, 9H), 1.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 199.0, 157.2, 155.0, 154.0, 146.2, 134.0, 133.0, 126.8, 124.1, 63.3, 62.9, 49.0, 43.0, 35.1, 31.4, 30.4, 29.9, 27.4, 14.1.

IR (neat): 2959, 2868,1736, 1680, 1465, 1426, 1362, 1258, 1238, 1180, 1131, 1066 cm^{-1}.

HRMS (ESI) calculated for $C_{21}H_{29}N_4O_3^+$ $[M+H]^+$ 385.2234, found 385.2229.

ethyl 2-(7-acetyl-5-(*tert*-butyl)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl)-2*H*-tetrazole-5-carboxylate (9):

Isolated Yield: 55%

Physical Property: White solid.

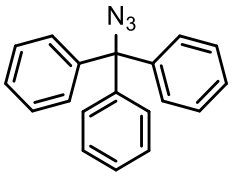
Melting Point: 149-151 ℃

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 6.85 (dd, *J* = 8.7, 3.7 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.70 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.49 (s, 3H), 2.34 (dd, *J* = 14.1, 3.7 Hz, 1H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.41 (s, 8H), 1.38 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 199.3, 158.2, 157.1, 155.4, 154.4, 134.2, 132.0, 126.5, 123.9, 67.2, 62.4, 48.8, 43.0, 35.1, 31.4, 29.9, 29.69, 27.5, 14.2.

IR (neat): 2960, 2869, 1743, 1683, 1466, 1361, 1233, 1203, 1065 cm^{-1}.

HRMS (ESI) calculated for $C_{21}H_{29}N_4O_3^+$ $[M+H]^+$ 385.2234, found 385.2227.

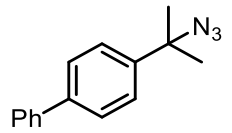


(azidomethanetriyl)tribenzene: According to Procedure A, a 4 mL borosilicate glass vial was charged with triphenylmethane (97.7 g, 0.40 mmol) 2.00 mol% of copper(II) acetate (1.50 mg, 8.00 μmol), 2.00 mol% of bathophenanthroline (2.70 mg, 8.00 μmol), 2.50 equivalents of *N*-fluorobenzenesulfonimide (315 mg, 1.00 mmol), and a magnetic stir bar outside a glovebox. The flask was capped with an open-top cap installed with a TFE lined silicone SURE-LINK^{TM} septum. The septum cap was pierced by a needle (22 gauge - 1 1/2", 0.7 mm x 40 mm) and the vial was moved into the glovebox and underwent four cycles of vacuum-nitrogen-backfill over 40 minutes. After removal of the needle, the vial was removed from the glovebox. The vial was charged with nitromethane (2.0 mL, 0.20 M) and 3.6 equivalents of azidotrimethylsilane (190 μL, 1.44 mmol) sequentially, stirred, and heated to 30 ℃ (inner temperature) in a heating block on a hot plate. After 16 hours, the vial was cooled to room temperature (25 ℃). All precipitates and catalysts were filtered out through a pipette-silica plug with dichloromethane (1.0 mL x 3 times). After evaporation of solvent on a rotary evaporator at 30 ℃, flash column chromatography (pentane) was performed. The isolated compound was dried to give 16 mg of trityl azide. ^{1}H and ^{13}C NMR spectrum of trityl azide was matched with the literature.[25,26]

Isolated Yield: 14%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.37 – 7.26 (m, 15H).
^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 143.1, 128.5, 128.2, 127.7, 77.1.



4-(2-azidopropan-2-yl)-1,1'-biphenyl: Prepared from 4-isopropyl-1,1'-biphenyl according to Procedure A. The reaction mixture was purified by flash column chromatography (diethyl ether:pentane = 1:30) to afford 26.7 mg of **4ab**.

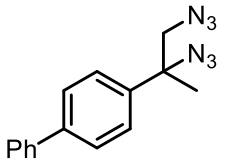
Isolated Yield: 28%

Physical Property: White solid.

Melting Point: 45-47 ℃.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.64 – 7.55 (m, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 2H), 7.39 – 7.31 (m, 1H), 1.68 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 143.8, 140.7, 140.4, 128.9, 127.5, 127.4, 127.2, 125.7, 63.8, 28.5.
IR (neat): 2974, 2103, 1487, 1247, 763 cm^{-1}.

HRMS (ESI) calculated for $C_{15}H_{15}^{+}$ $[M-N_3]^{+}$ 195.1168, found 195.1168.



4-(1,2-diazidopropan-2-yl)-1,1'-biphenyl: Prepared from 4-isopropyl-1,1'-biphenyl according to Procedure A. The reaction mixture was purified by flash column chromatography (diethyl ether:pentane = 1:30) to afford 13.5 mg of **4ab**.

Isolated Yield: 12%

Physical Property: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 7.67 – 7.56 (m, 4H), 7.55 – 7.41 (m, 4H), 7.40 – 7.32 (m, 1H), 3.54 (d, J = 12.5 Hz, 1H), 3.44 (d, J = 12.5 Hz, 1H), 1.80 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$ containing 1 % (v/v) TMS) δ 141.3, 140.4, 139.7, 129.0, 127.8, 127.7, 127.3, 126.4, 66.6, 61.1, 22.5.

IR (neat): 2981, 2101, 1294, 1249, 833 cm^{-1}.

HRMS (ESI) calculated for $C_{14}H_{13}^{+}$ $[M-N_3-CH_2N_3+H]^{+}$ 181.1012, found 181.1011.

11. References

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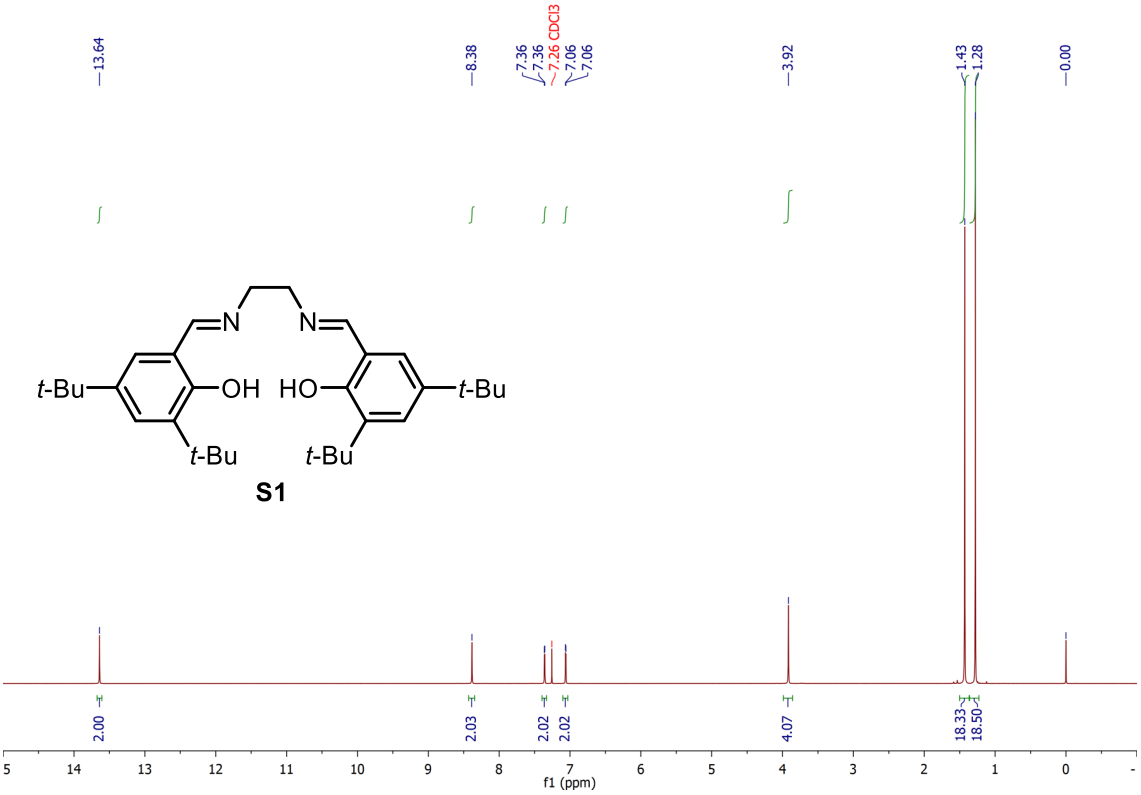
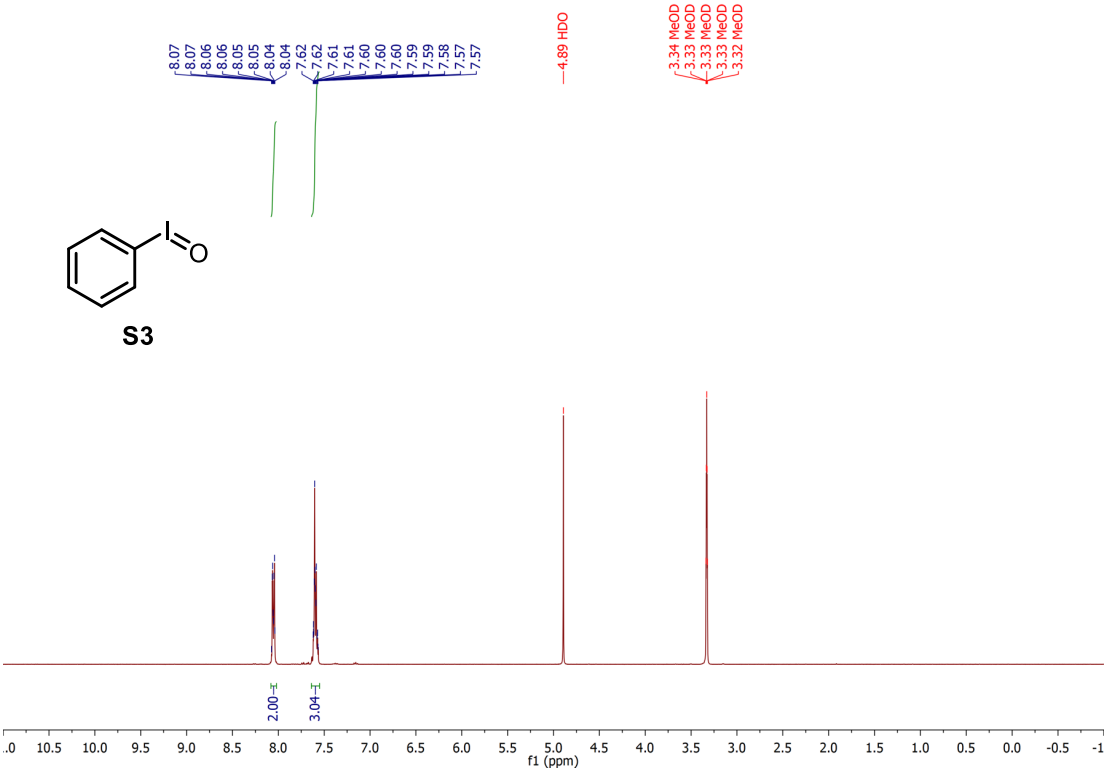
12. NMR Spectra of Characterized Compounds

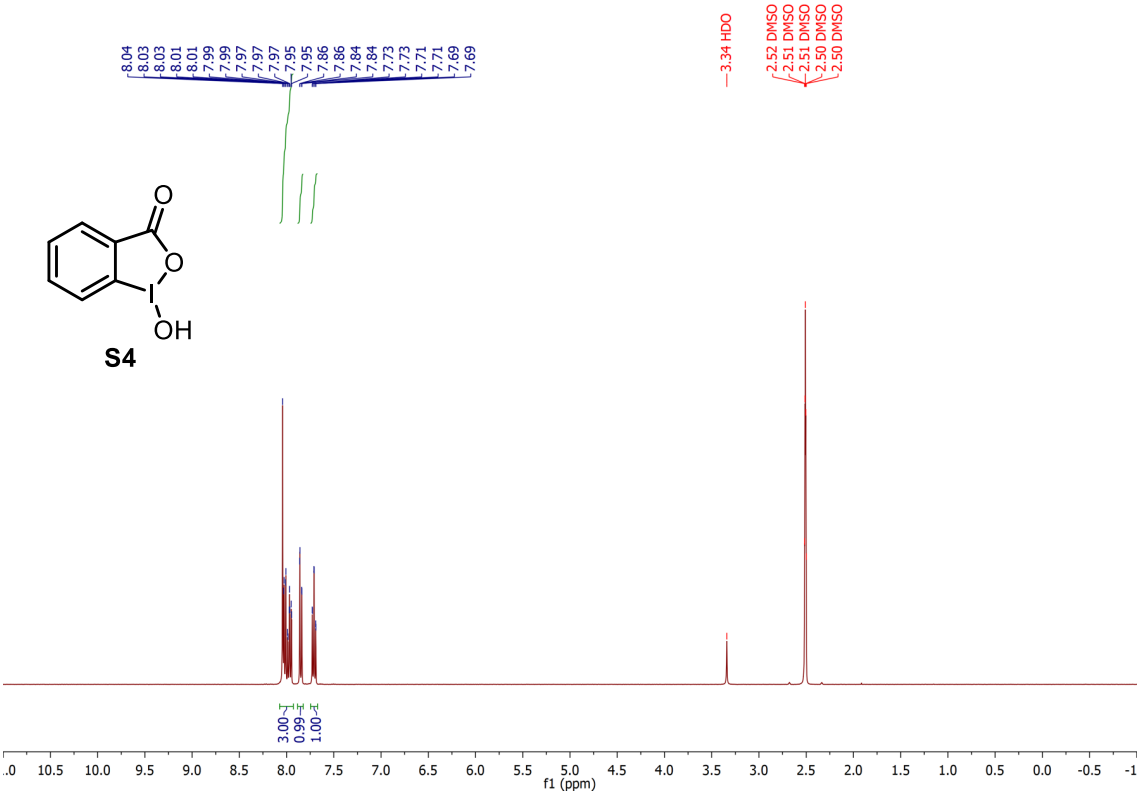
^{1}H NMR spectrum of **S1** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



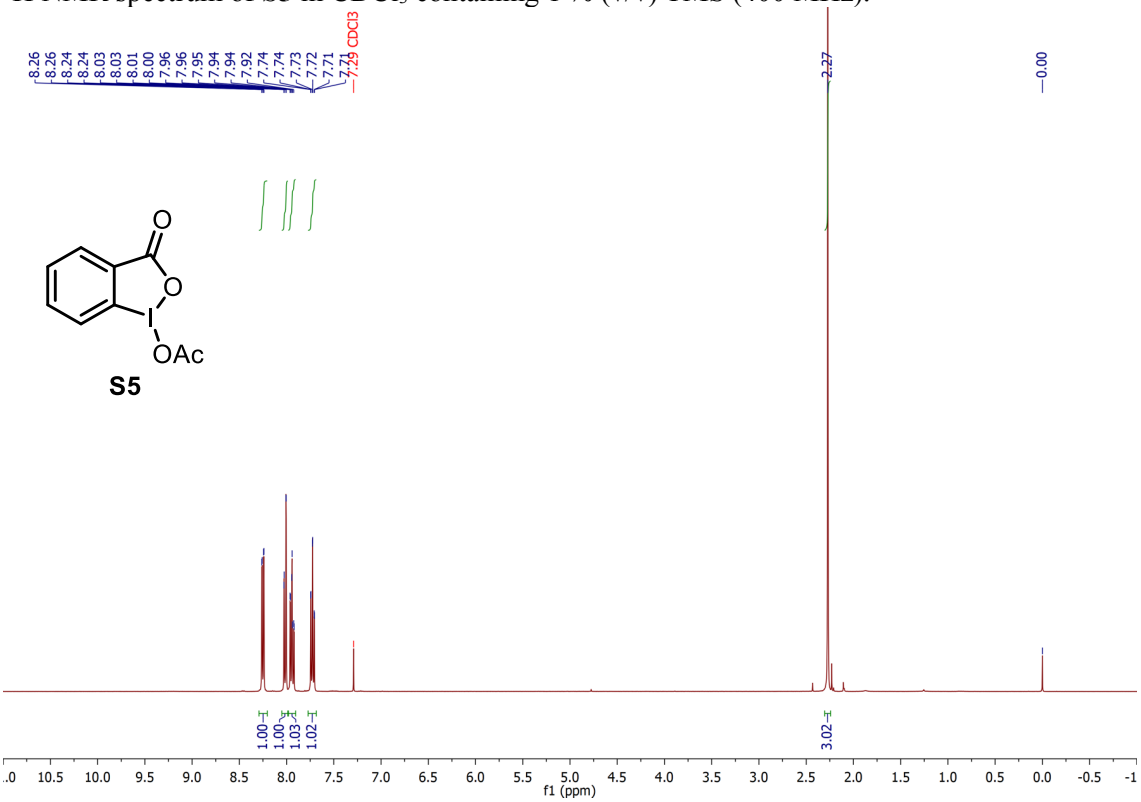
^{1}H NMR spectrum of **S3** in MeOD (400 MHz).



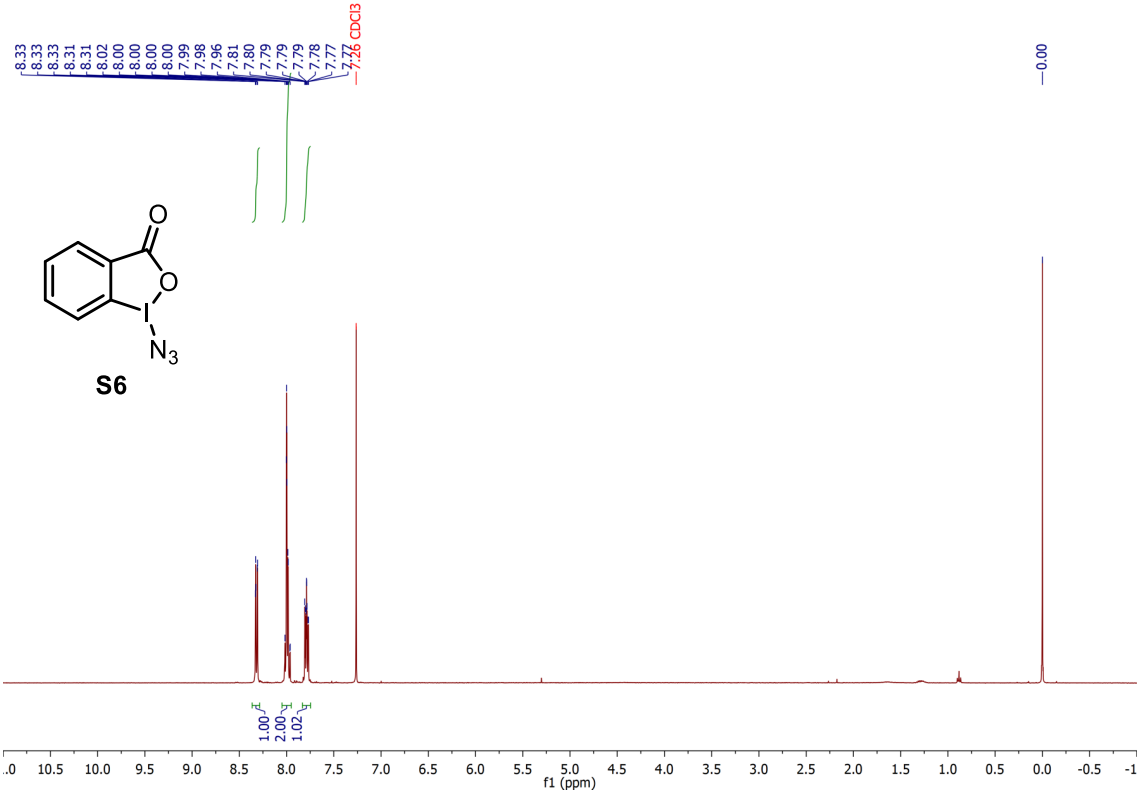
^{1}H NMR spectrum of **S4** in DMSO-d_6 (400 MHz).



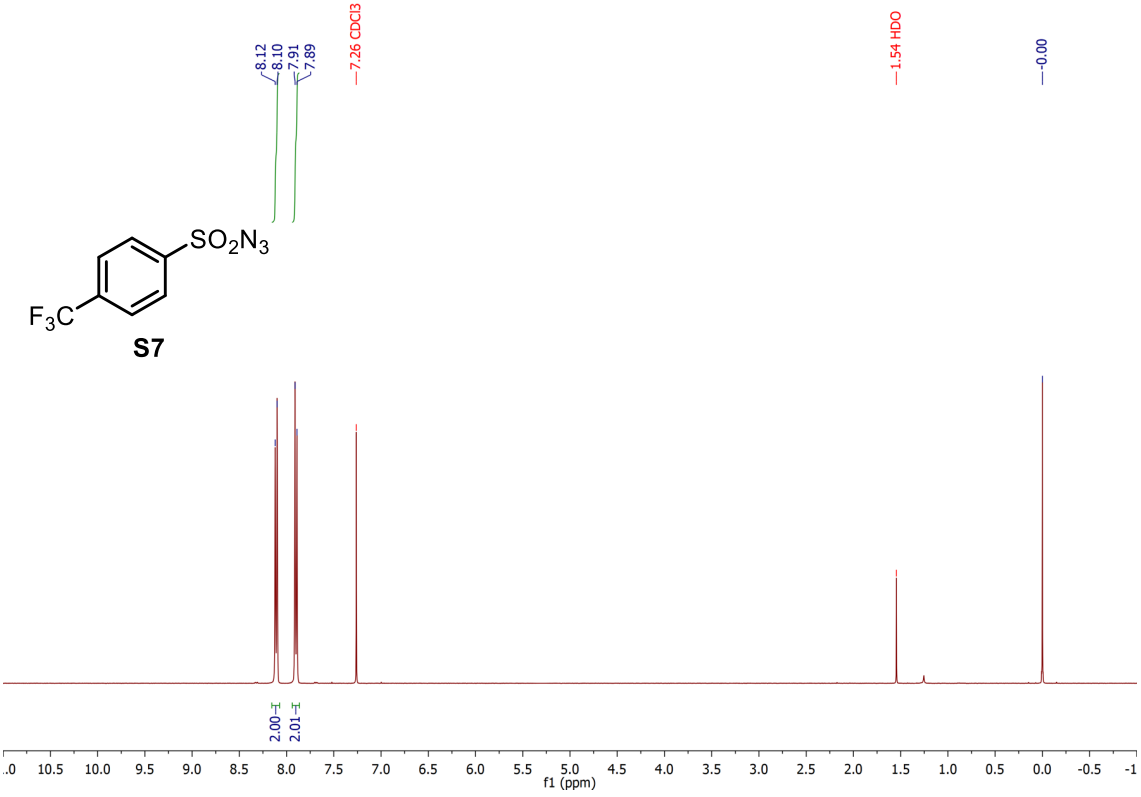
^{1}H NMR spectrum of **S5** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



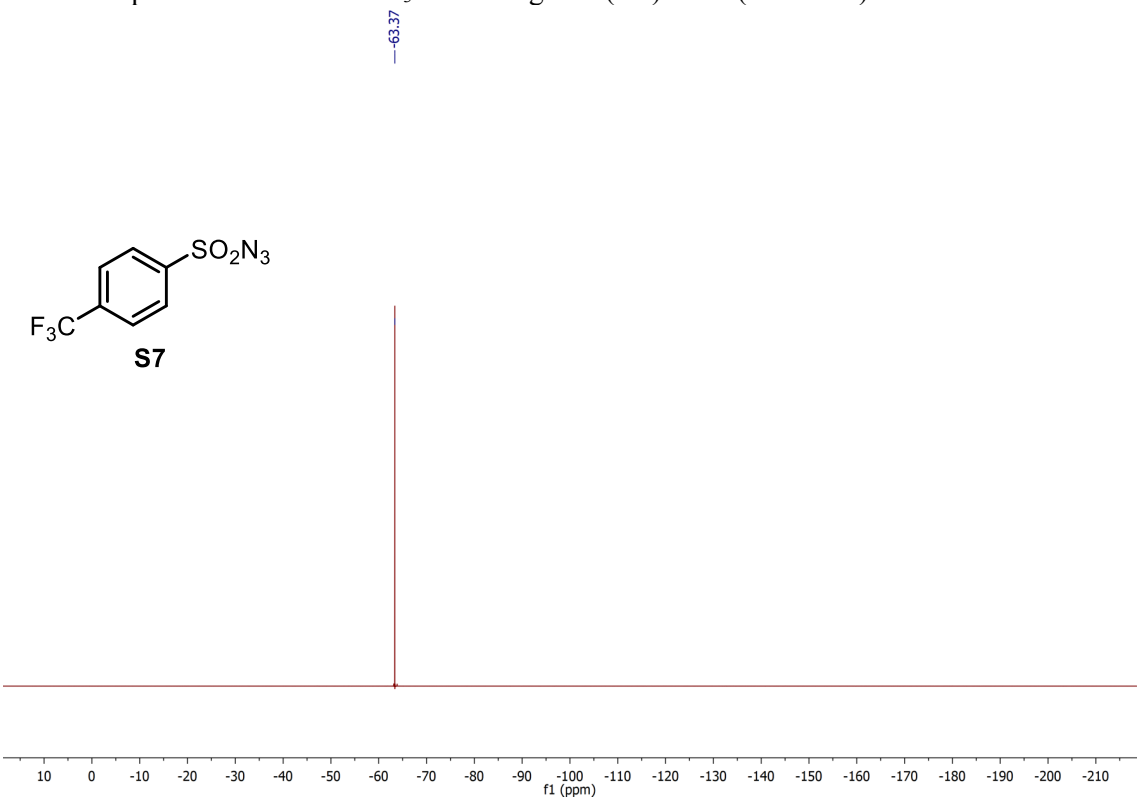
^{1}H NMR spectrum of **S6** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



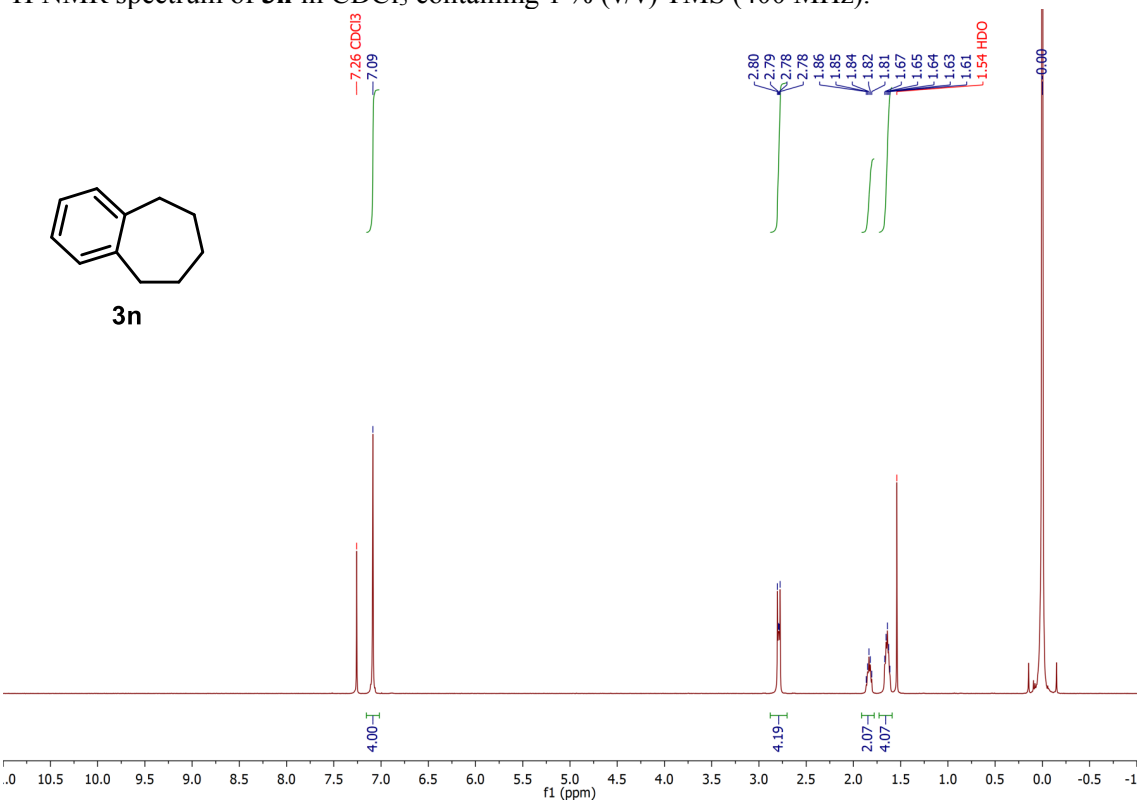
^{1}H NMR spectrum of **S7** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



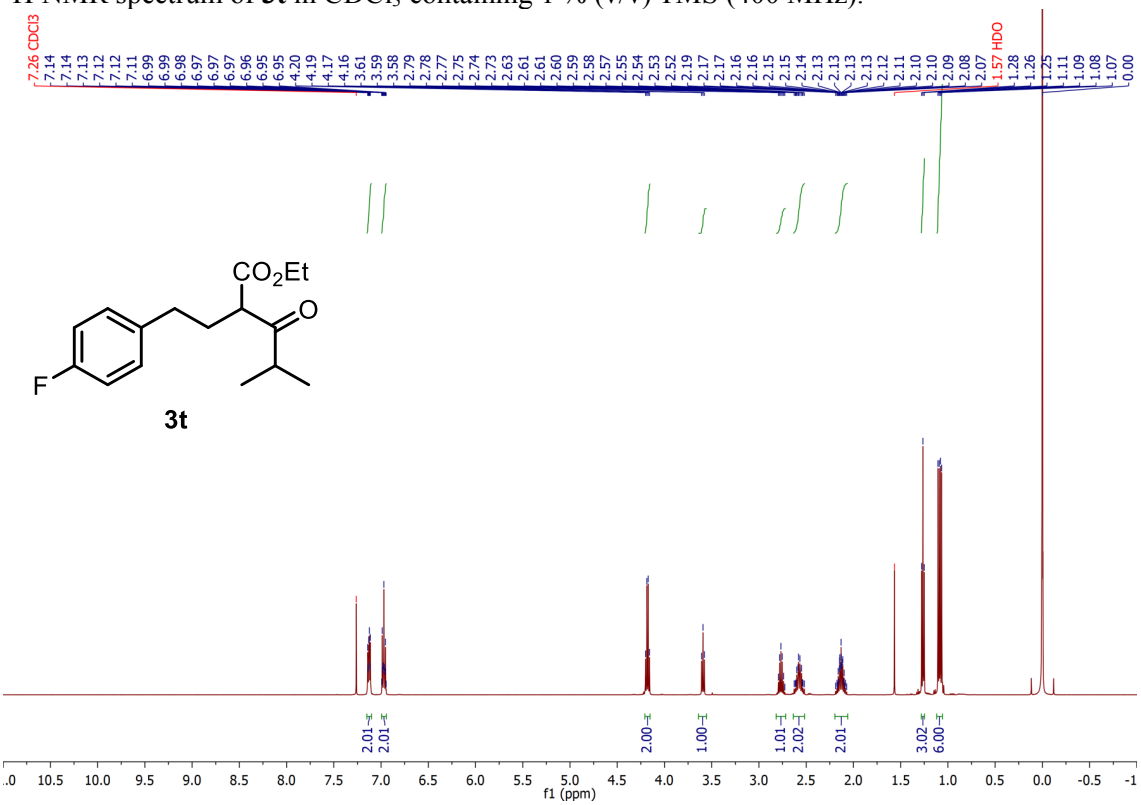
^{19}F NMR spectrum of **S7** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



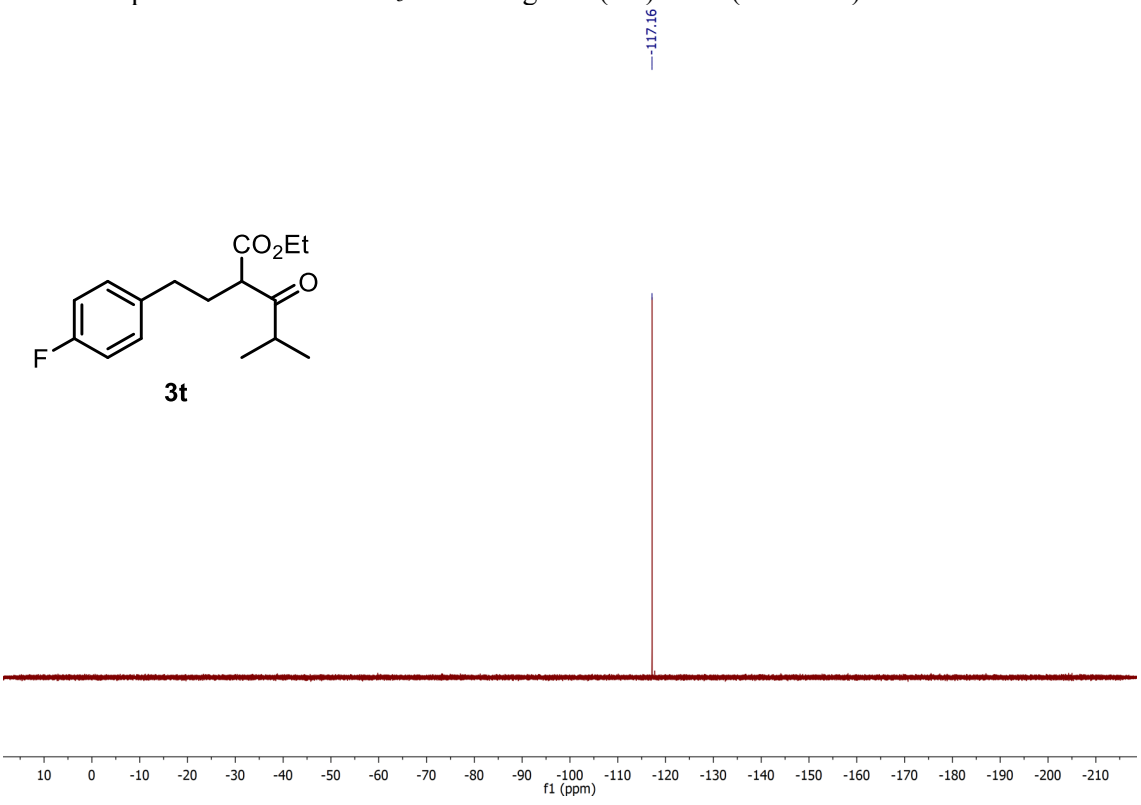
^{1}H NMR spectrum of **3n** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



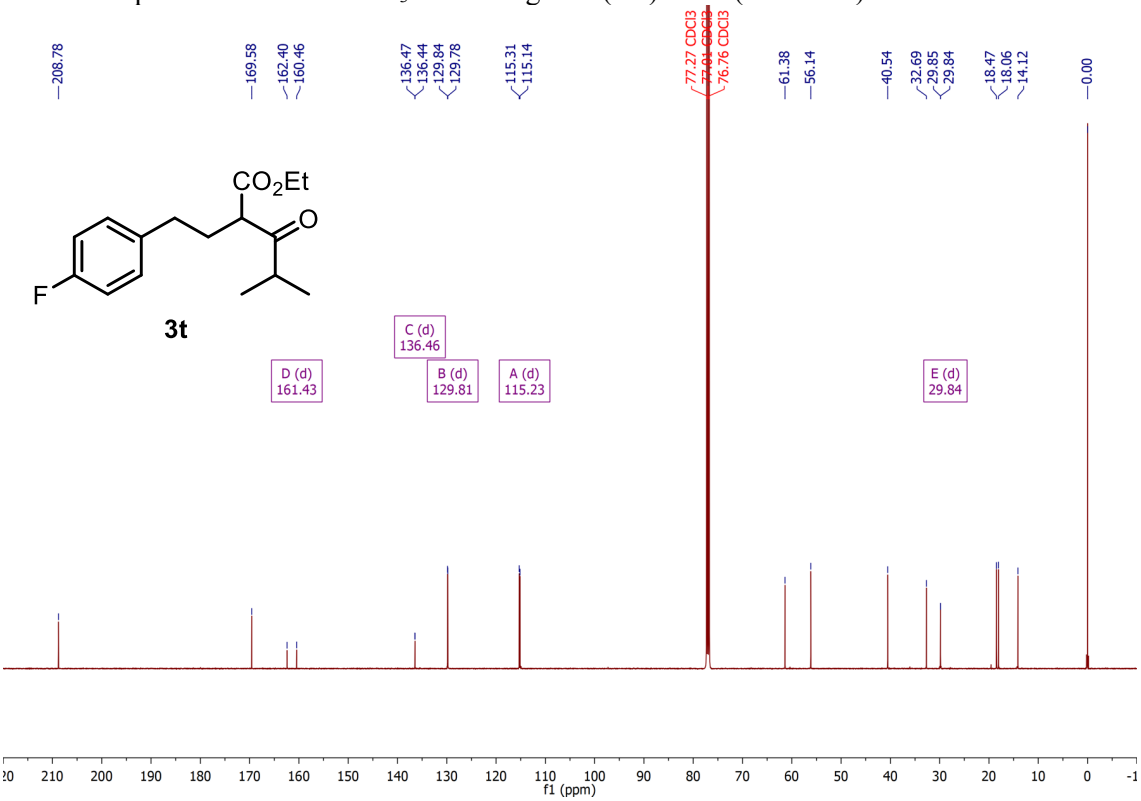
^{1}H NMR spectrum of **3t** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



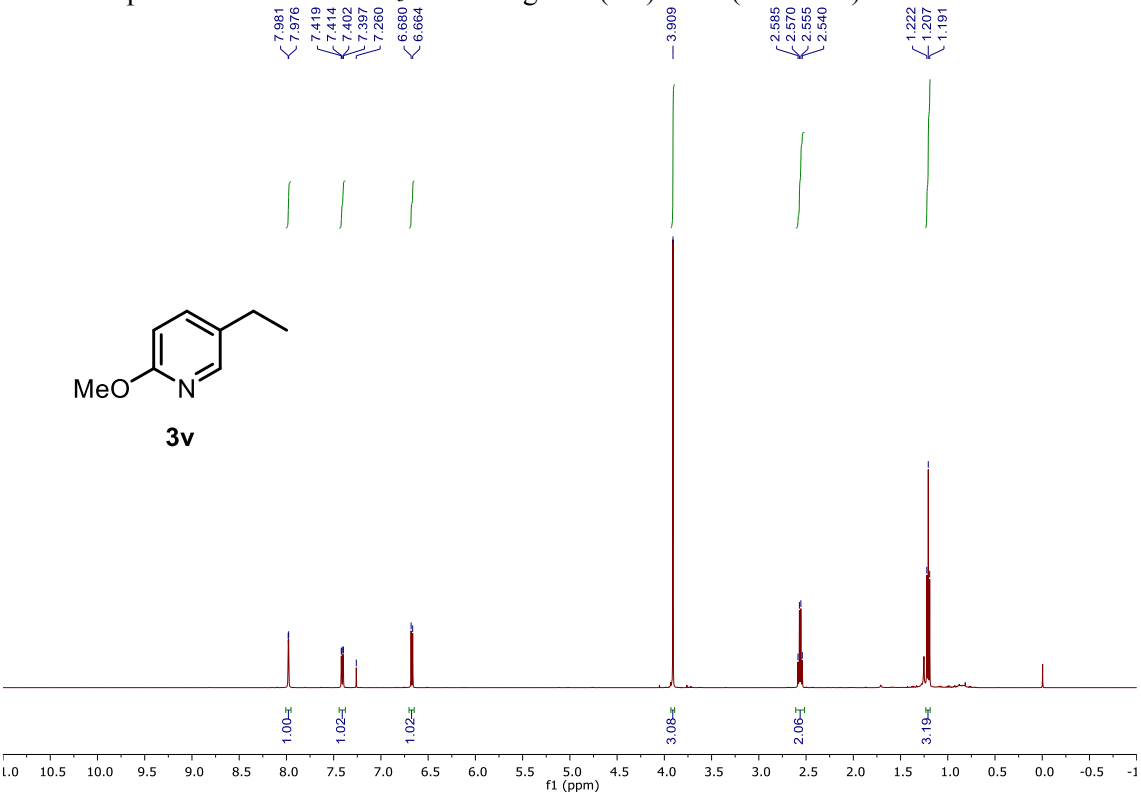
^{19}F NMR spectrum of **3t** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



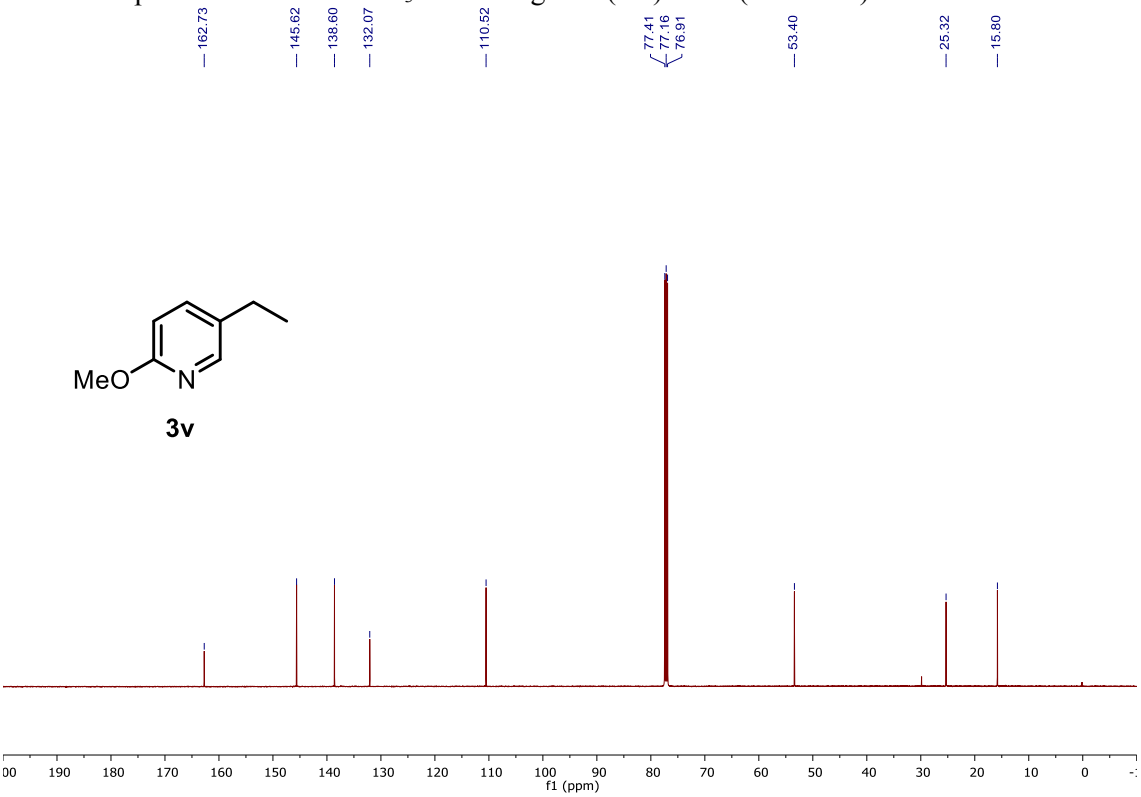
^{13}C NMR spectrum of **3t** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



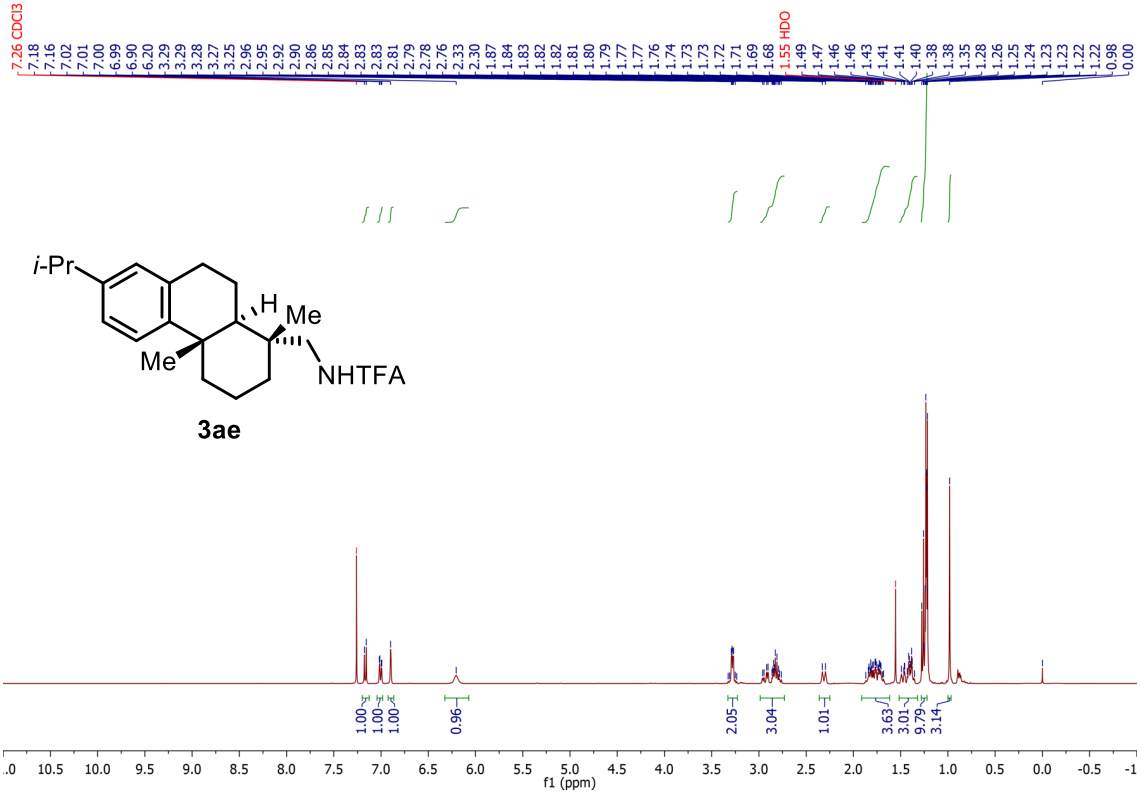
^{1}H NMR spectrum of **3v** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



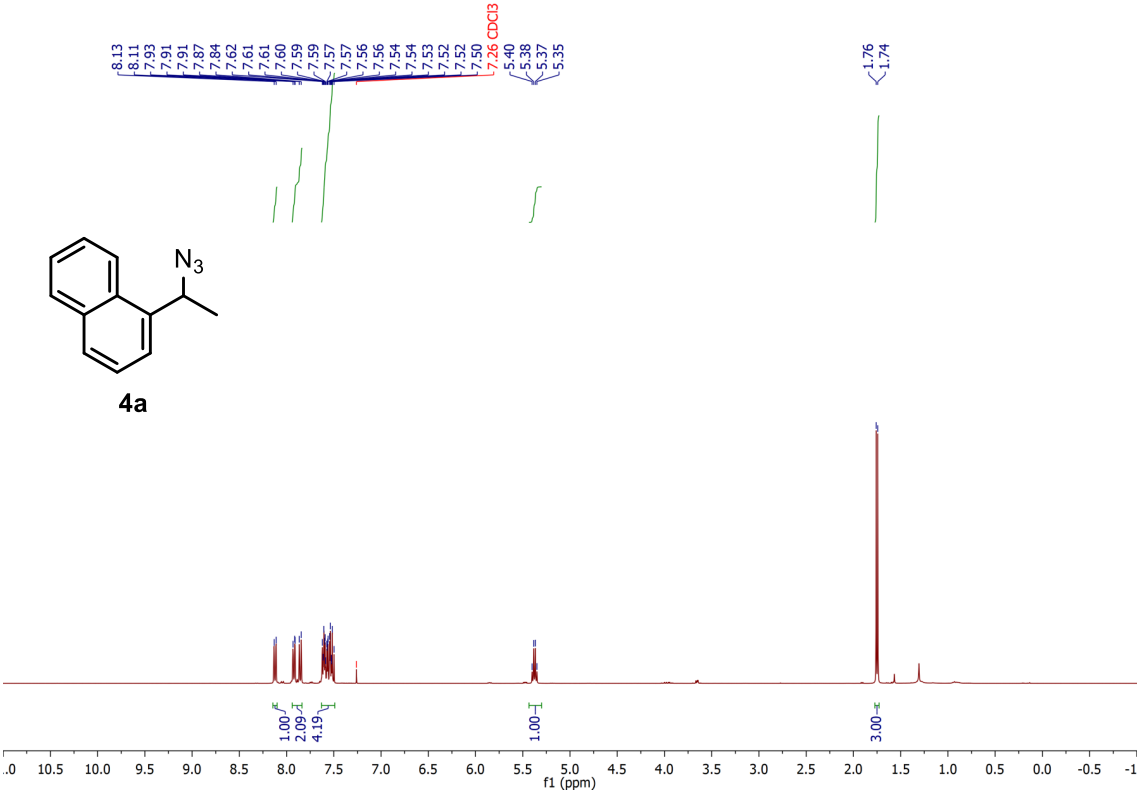
^{13}C NMR spectrum of **3v** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



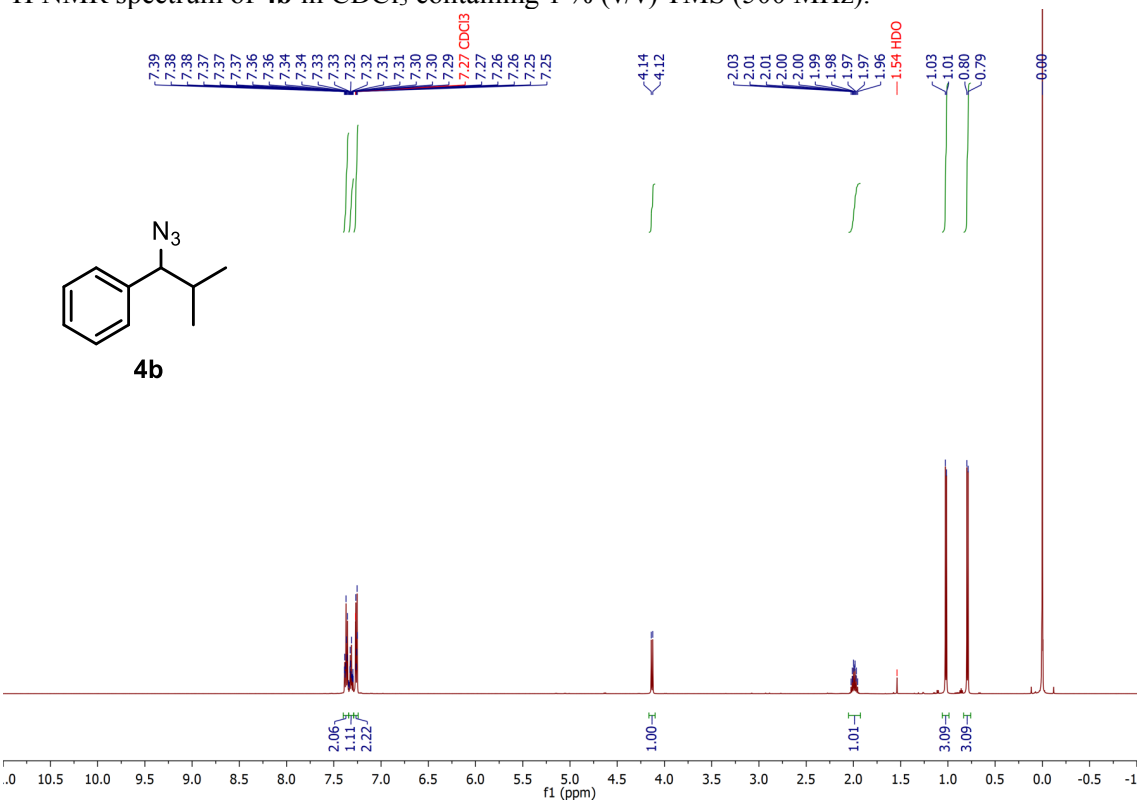
^{1}H NMR spectrum of **3ae** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



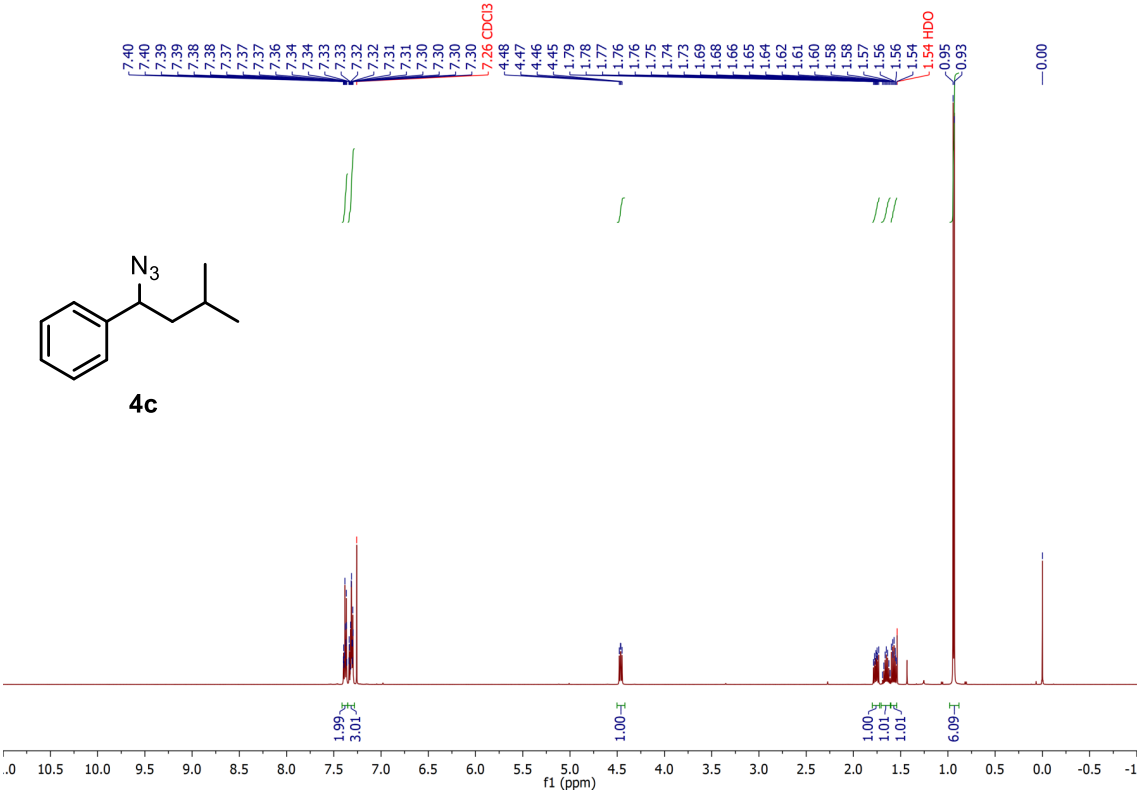
^{1}H NMR spectrum of **4a** in $CDCl_3$ (400 MHz).



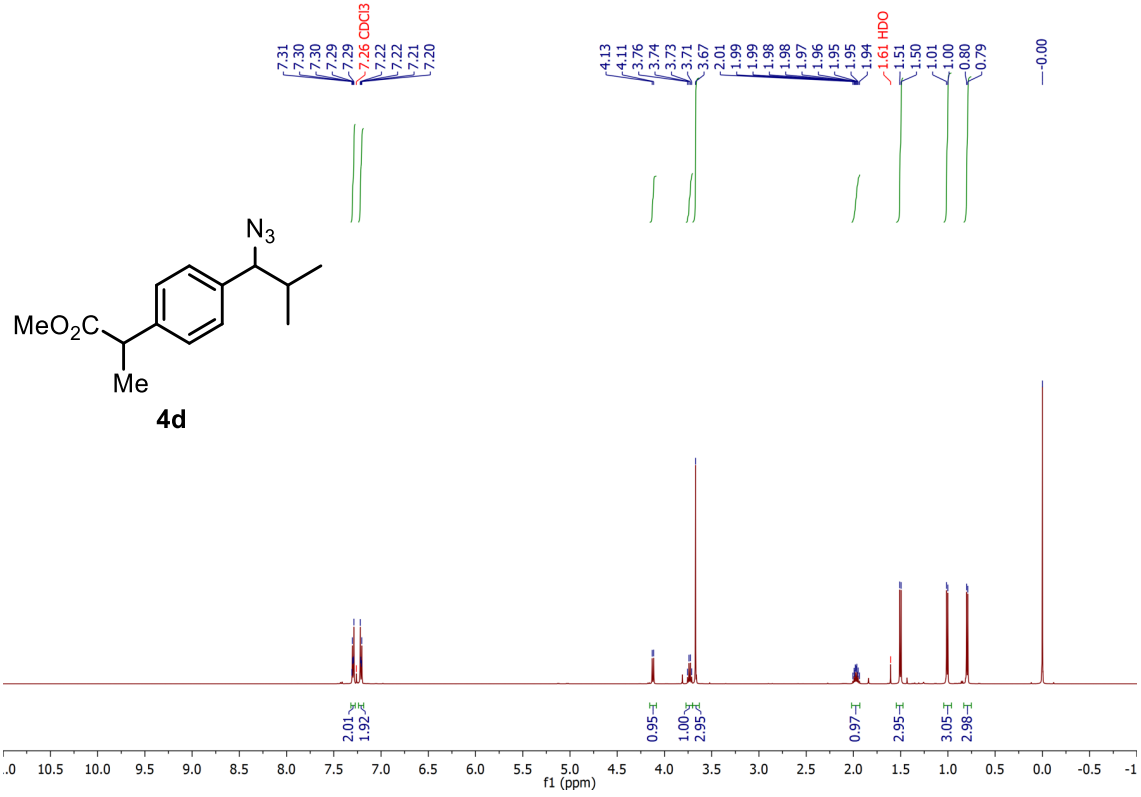
^{1}H NMR spectrum of **4b** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



^{1}H NMR spectrum of **4c** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



^{1}H NMR spectrum of **4d** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



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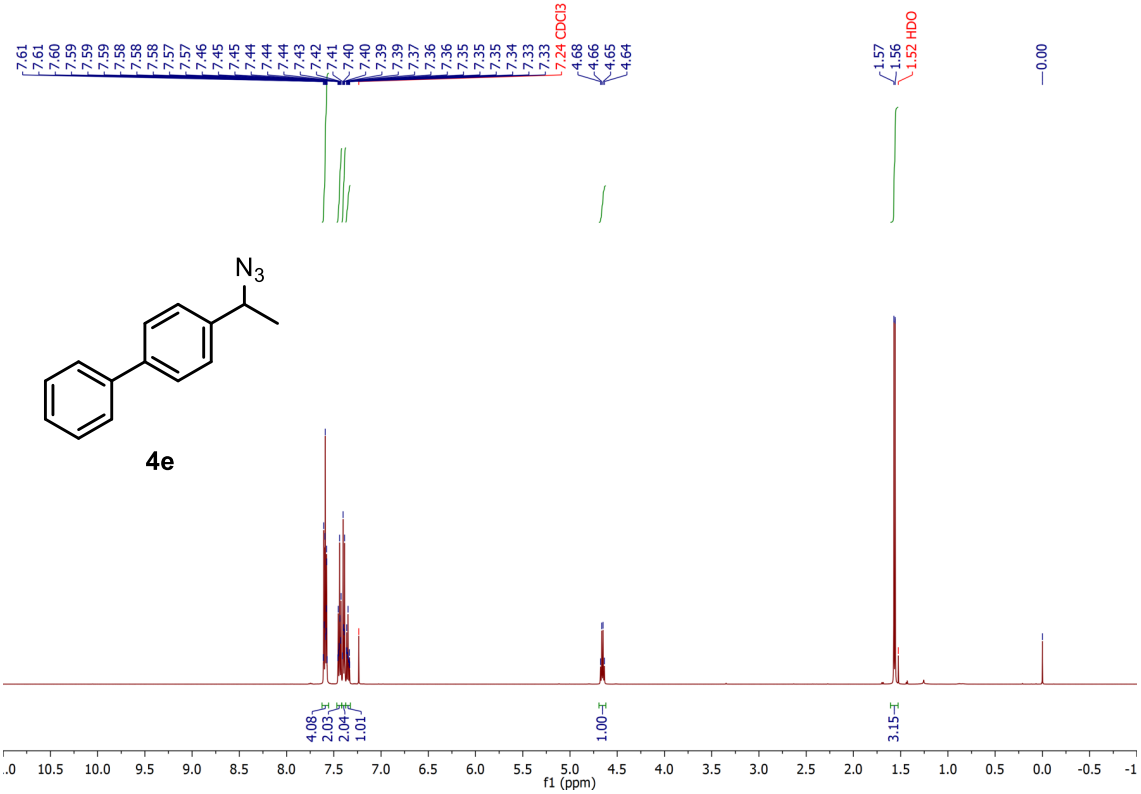
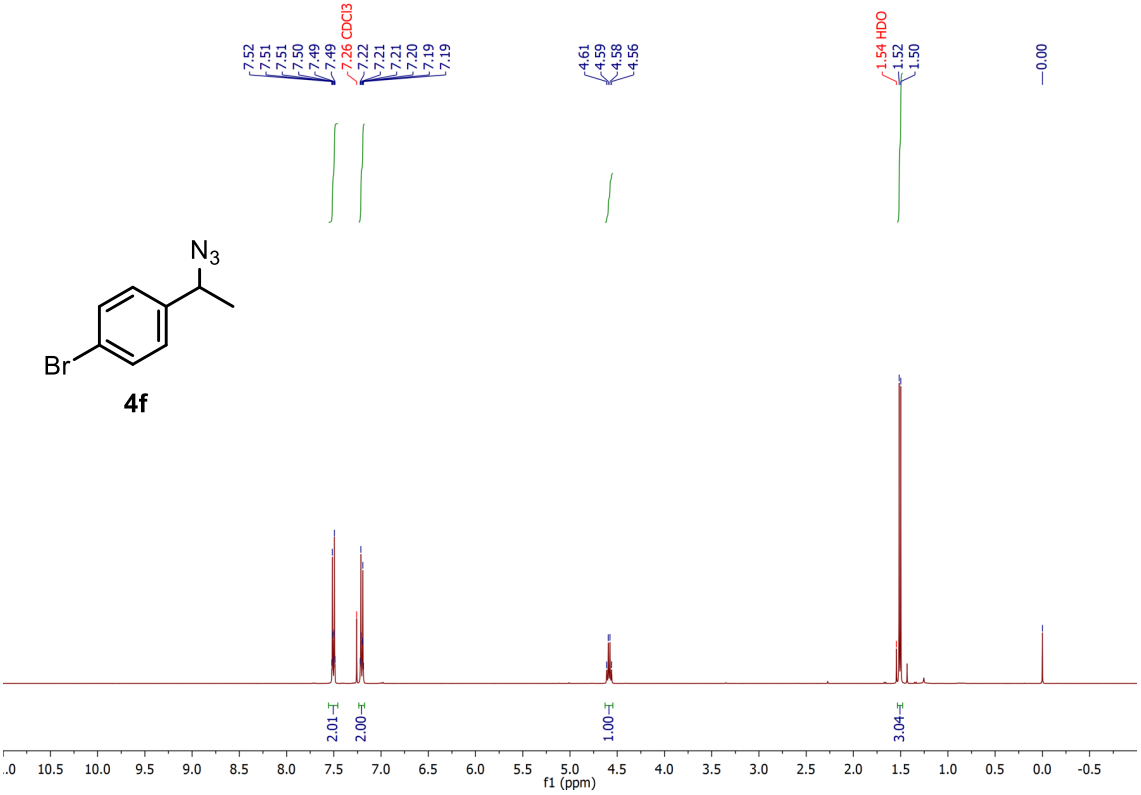
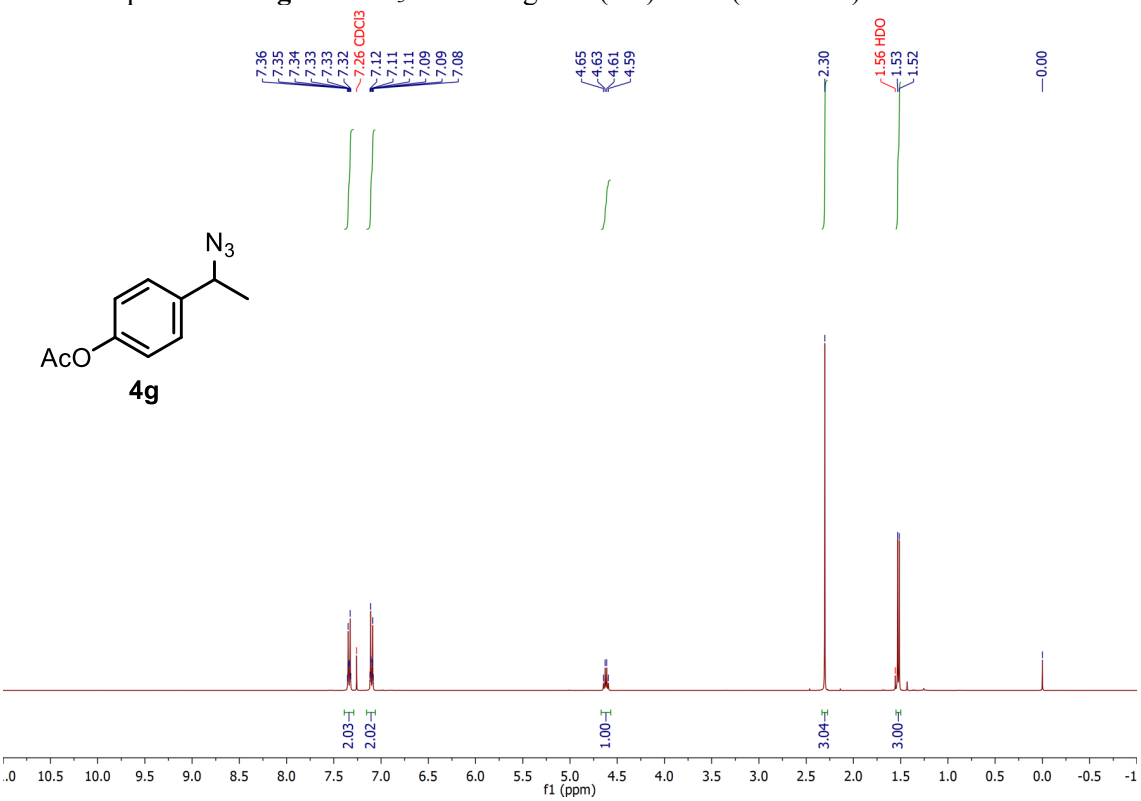


^{1}H NMR spectrum of **4f** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



^{1}H NMR spectrum of **4g** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



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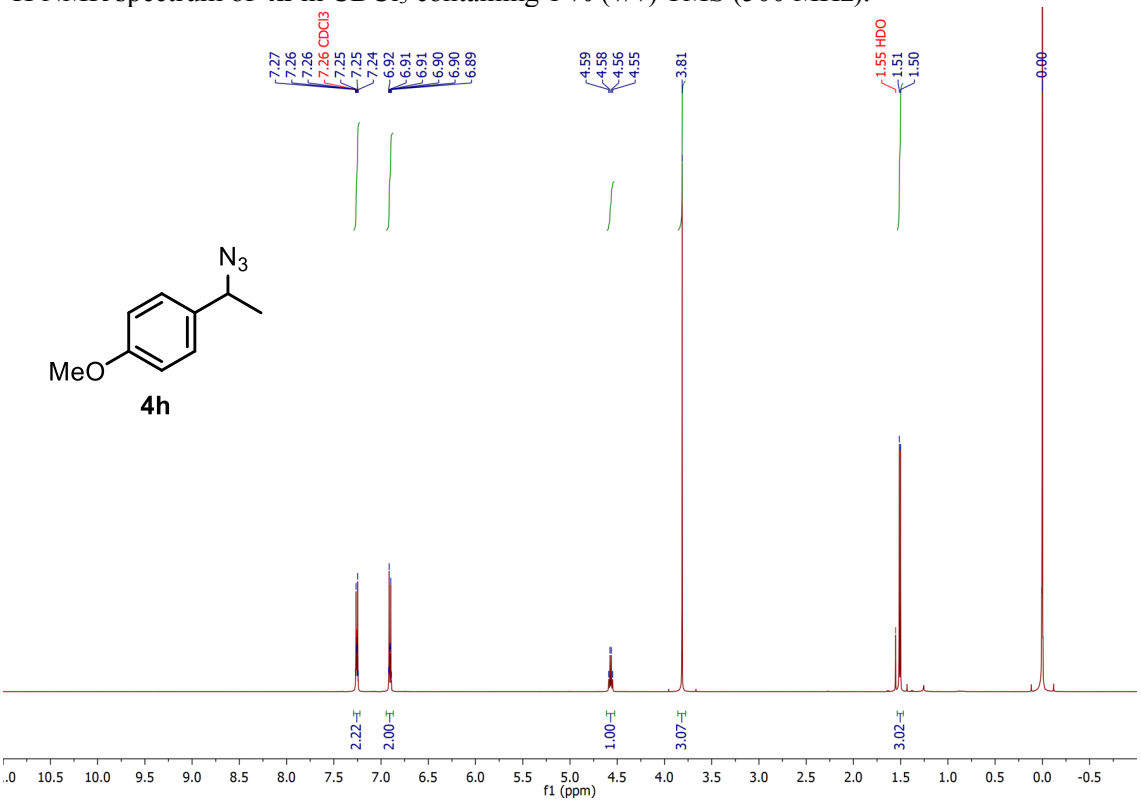
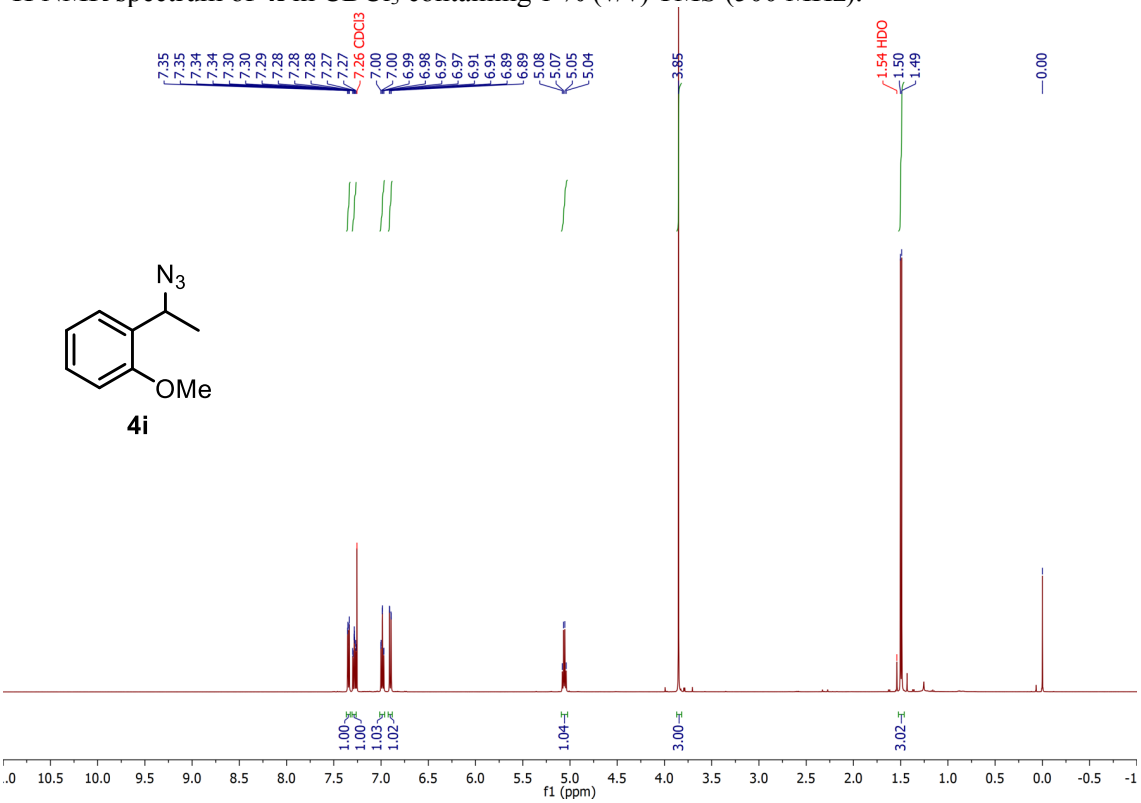
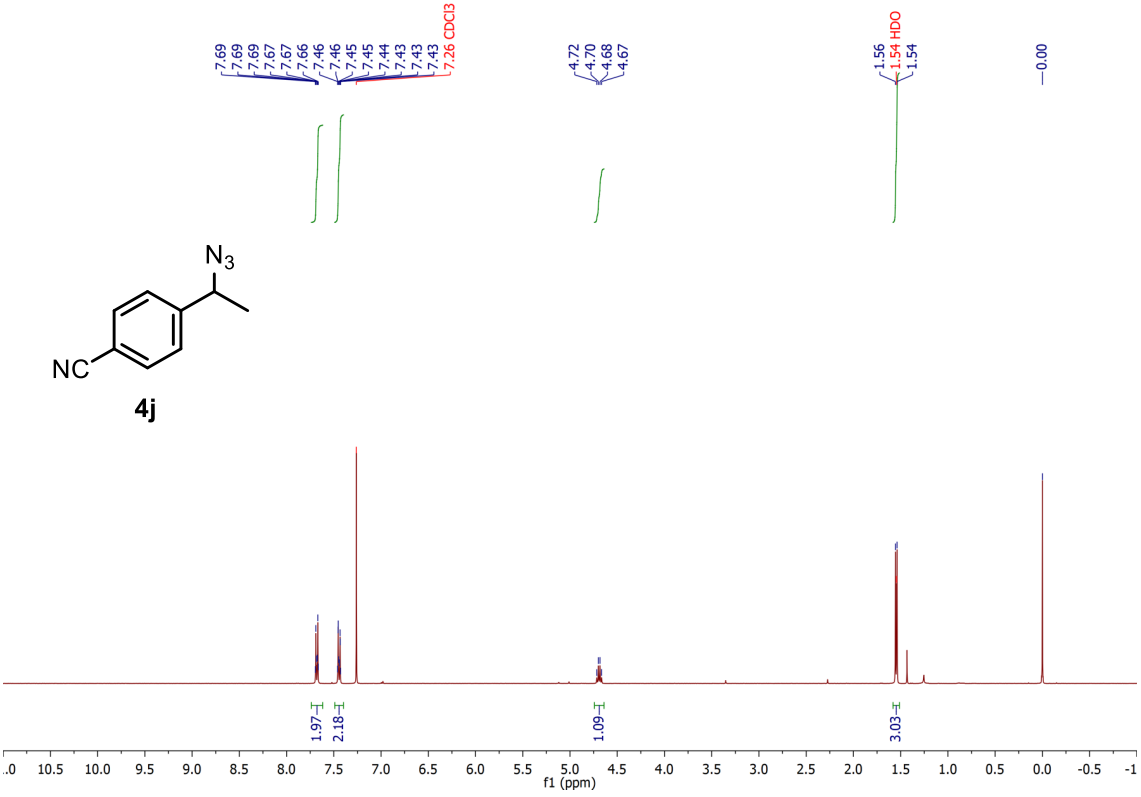


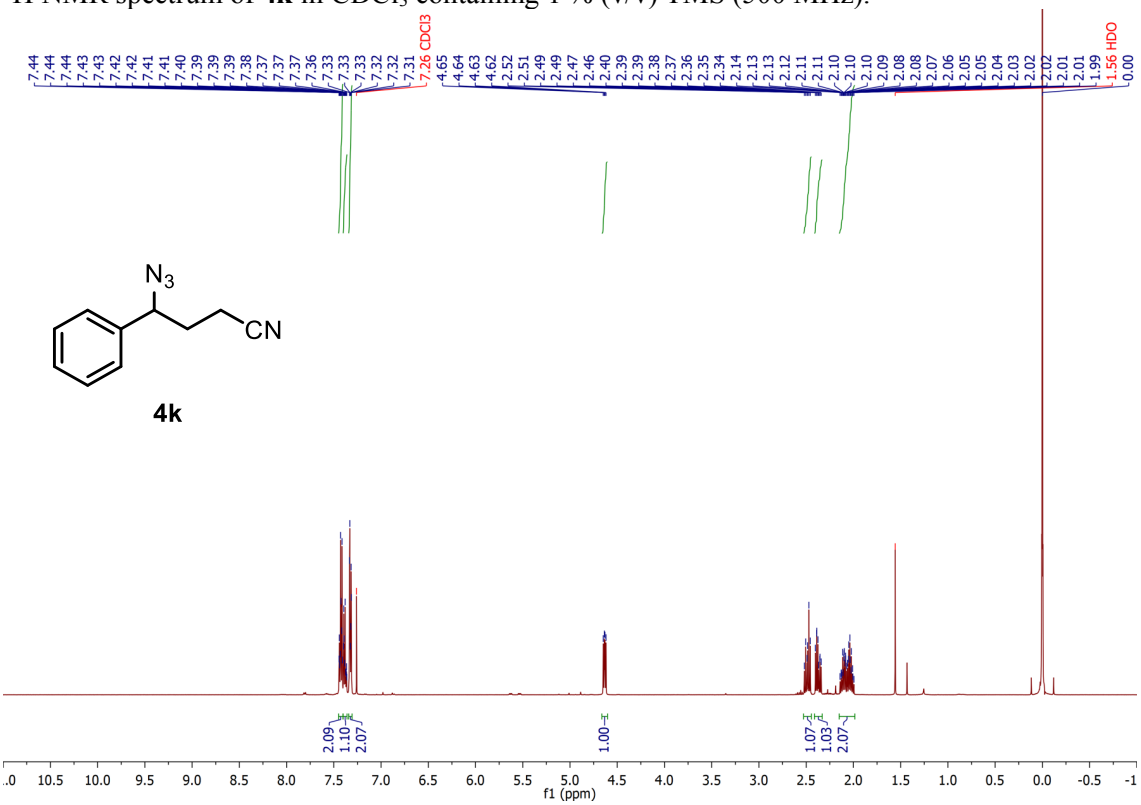
^{1}H NMR spectrum of **4i** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



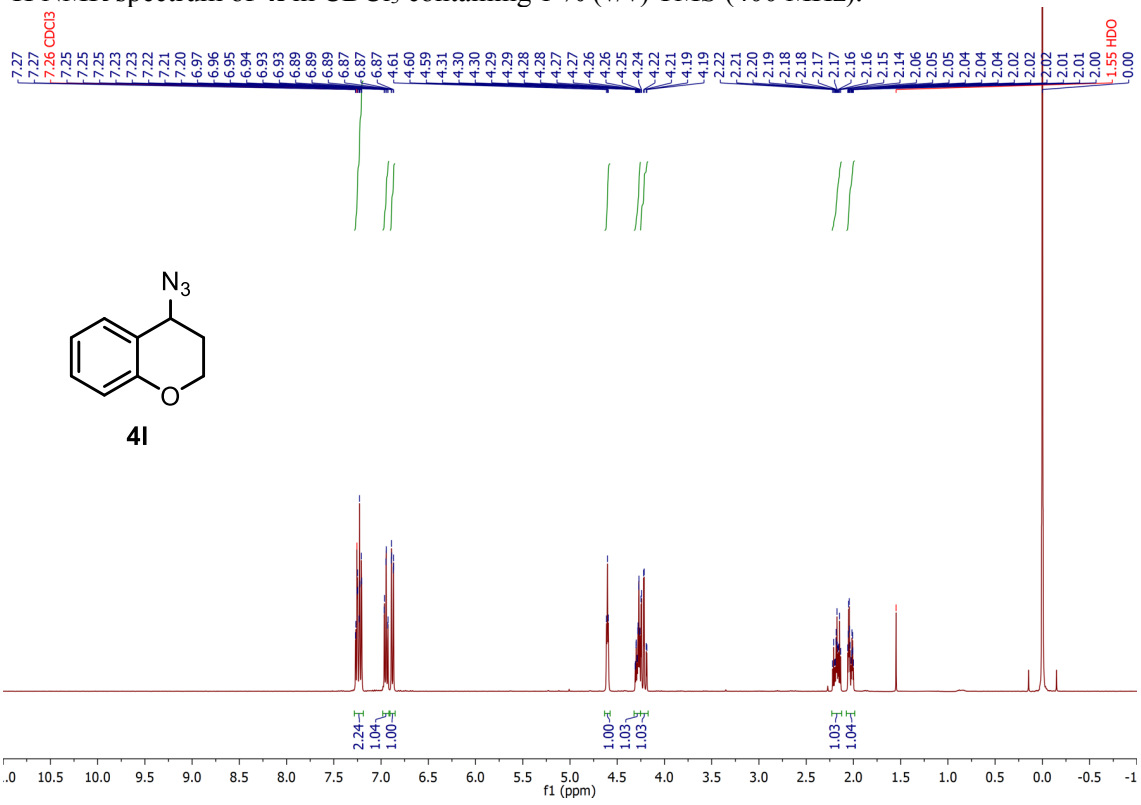
^{1}H NMR spectrum of **4j** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



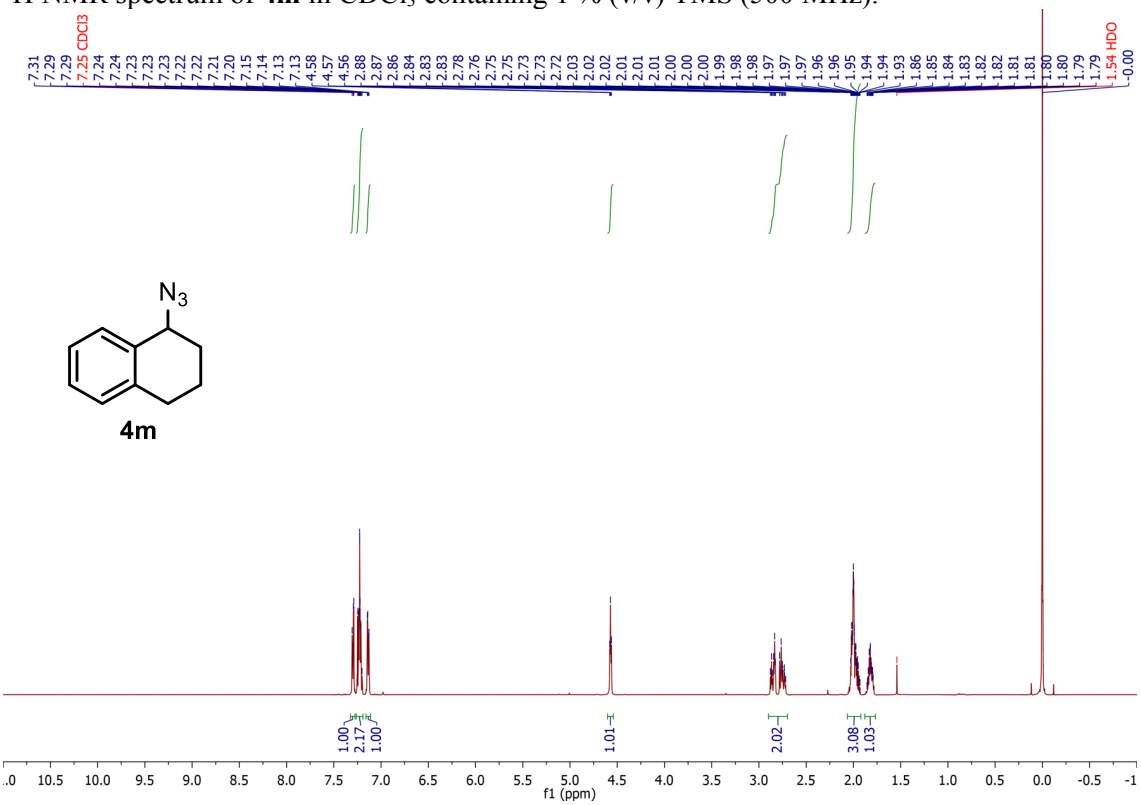
^{1}H NMR spectrum of **4k** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



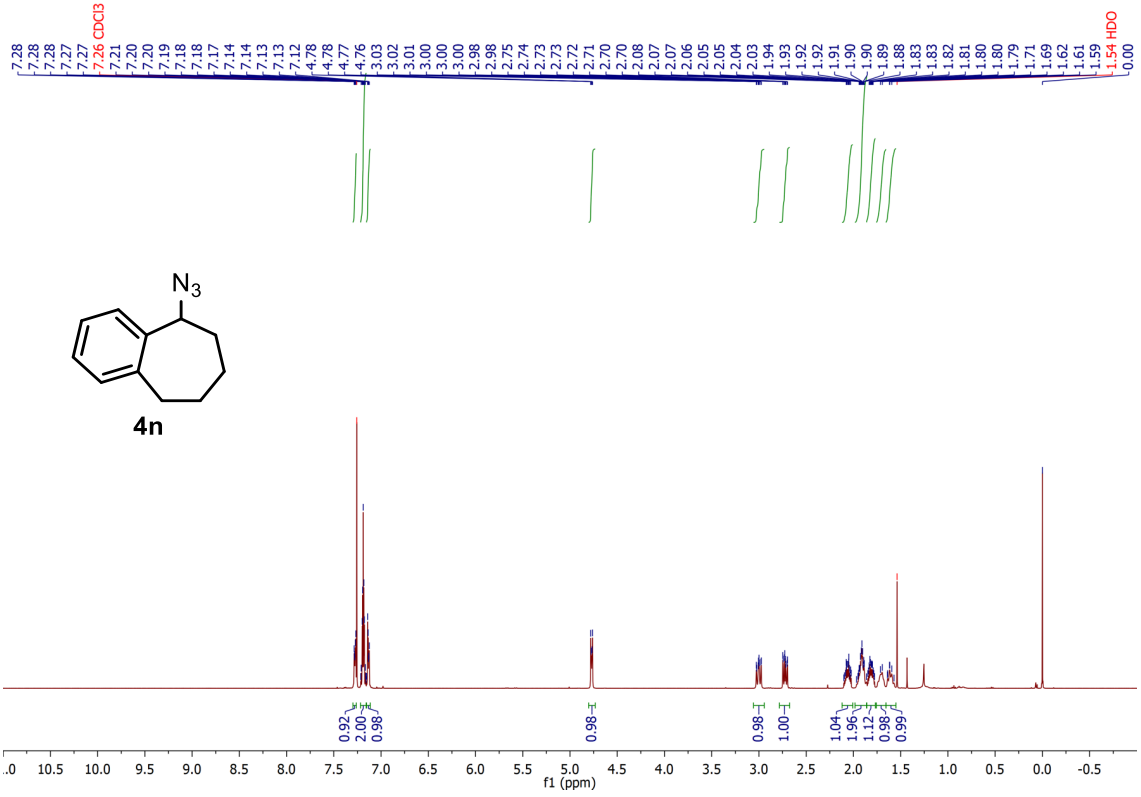
^{1}H NMR spectrum of **4l** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



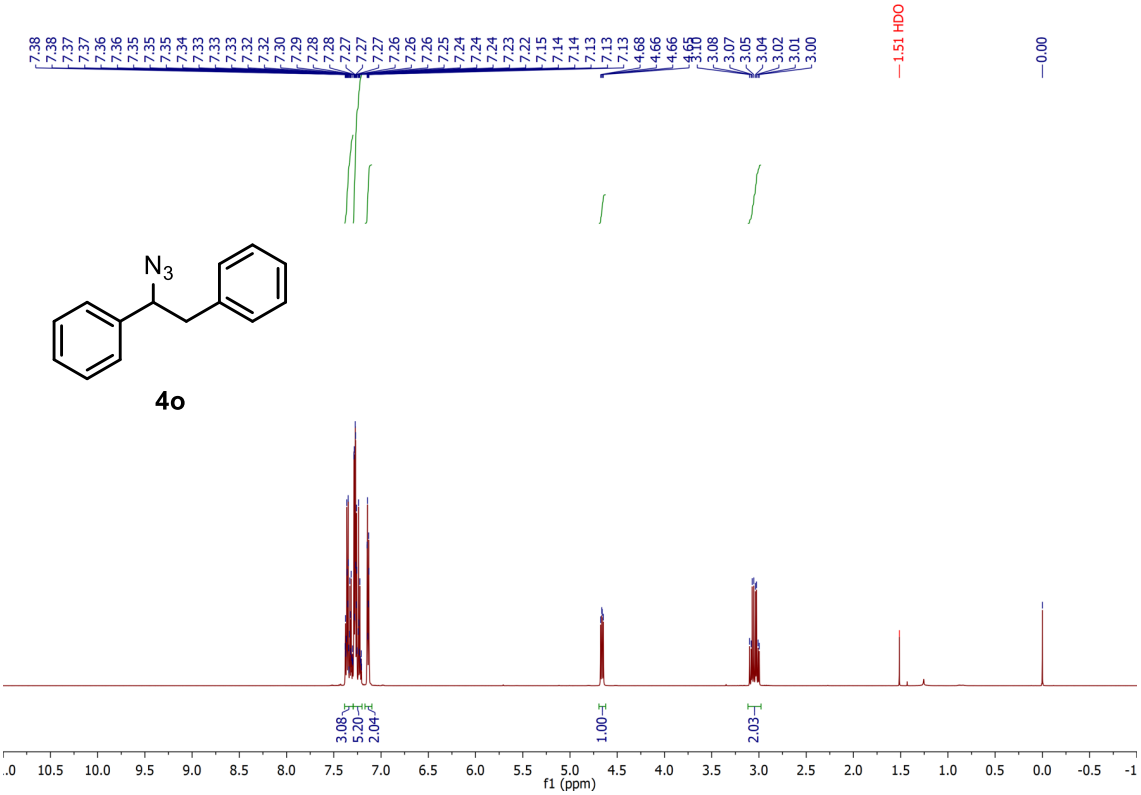
^{1}H NMR spectrum of **4m** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



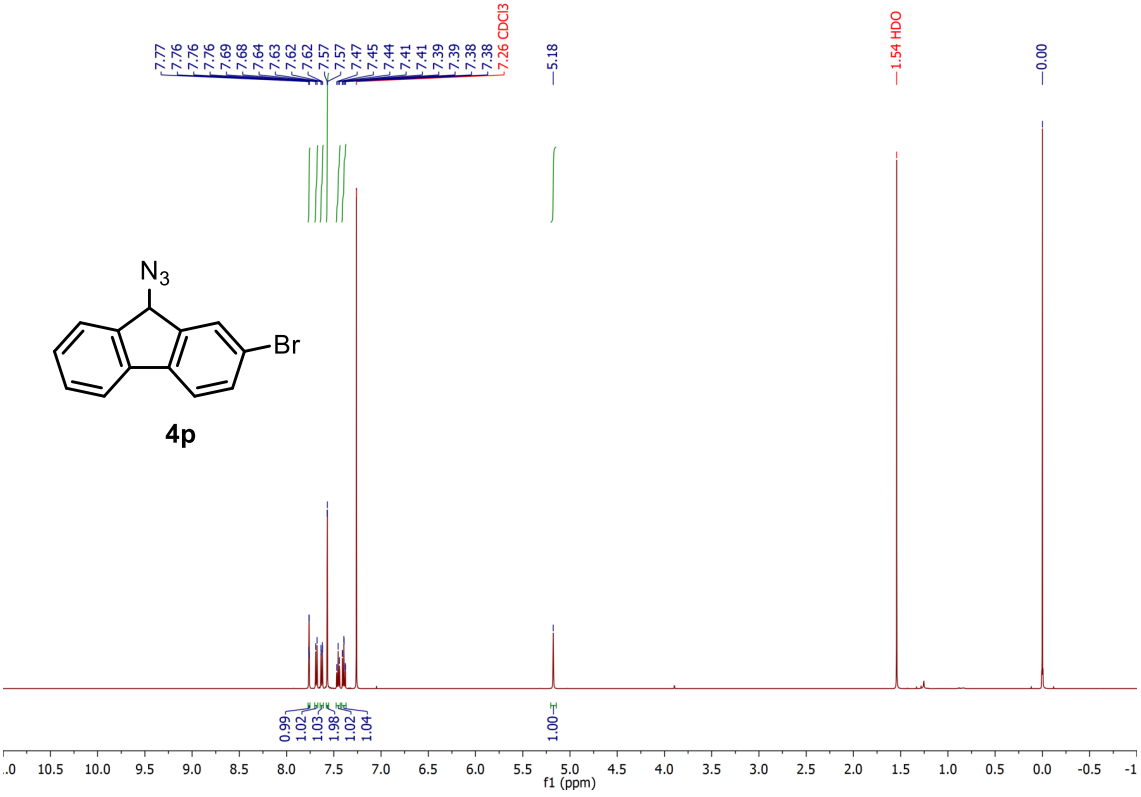
^{1}H NMR spectrum of **4n** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



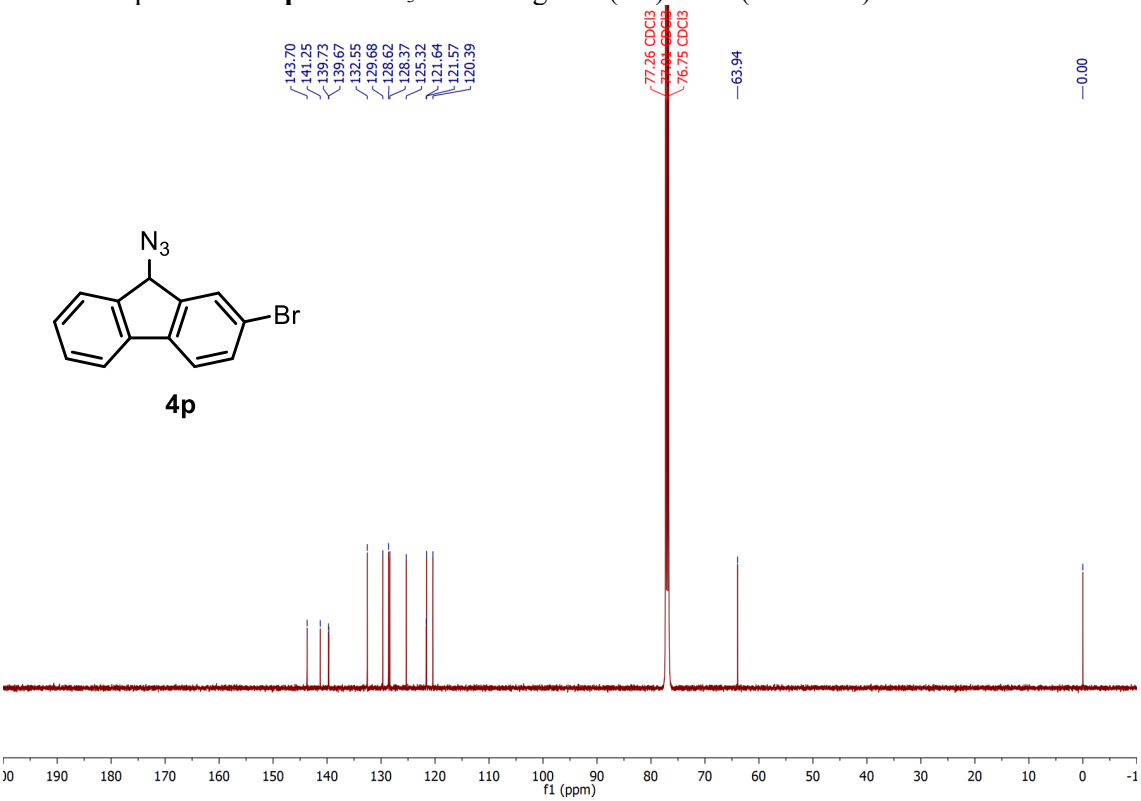
^{1}H NMR spectrum of **4o** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



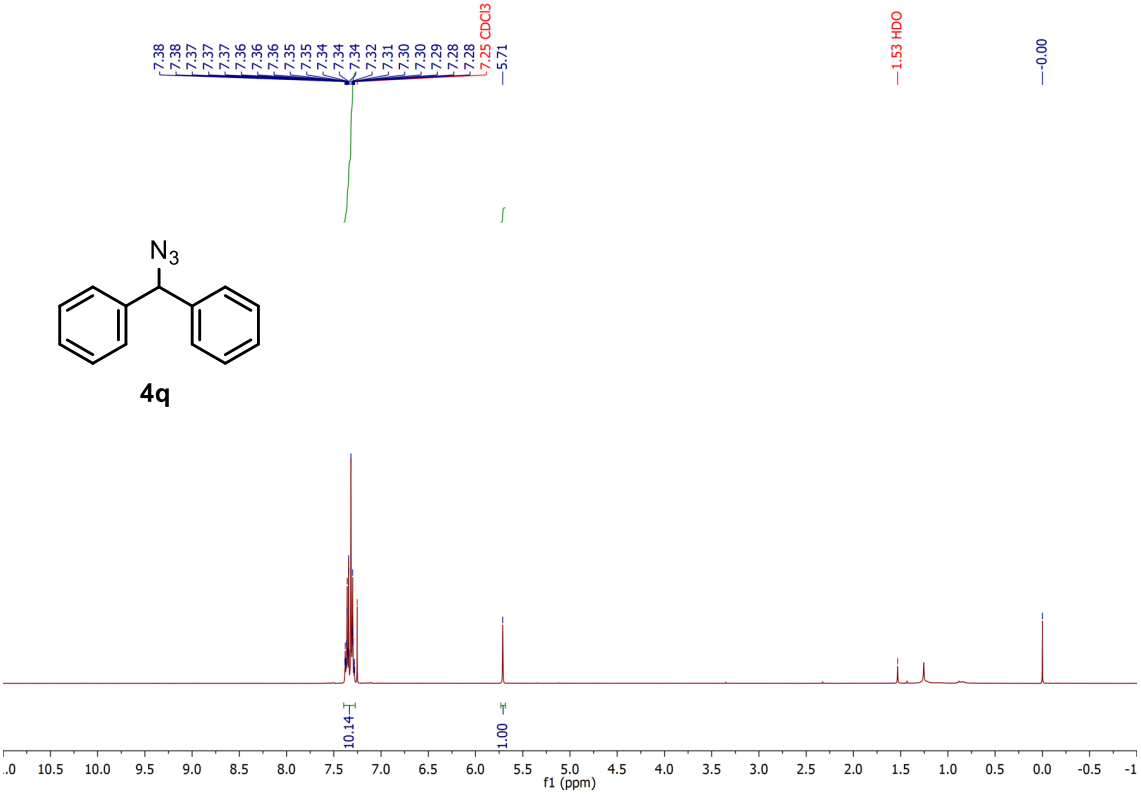
^{1}H NMR spectrum of **4p** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



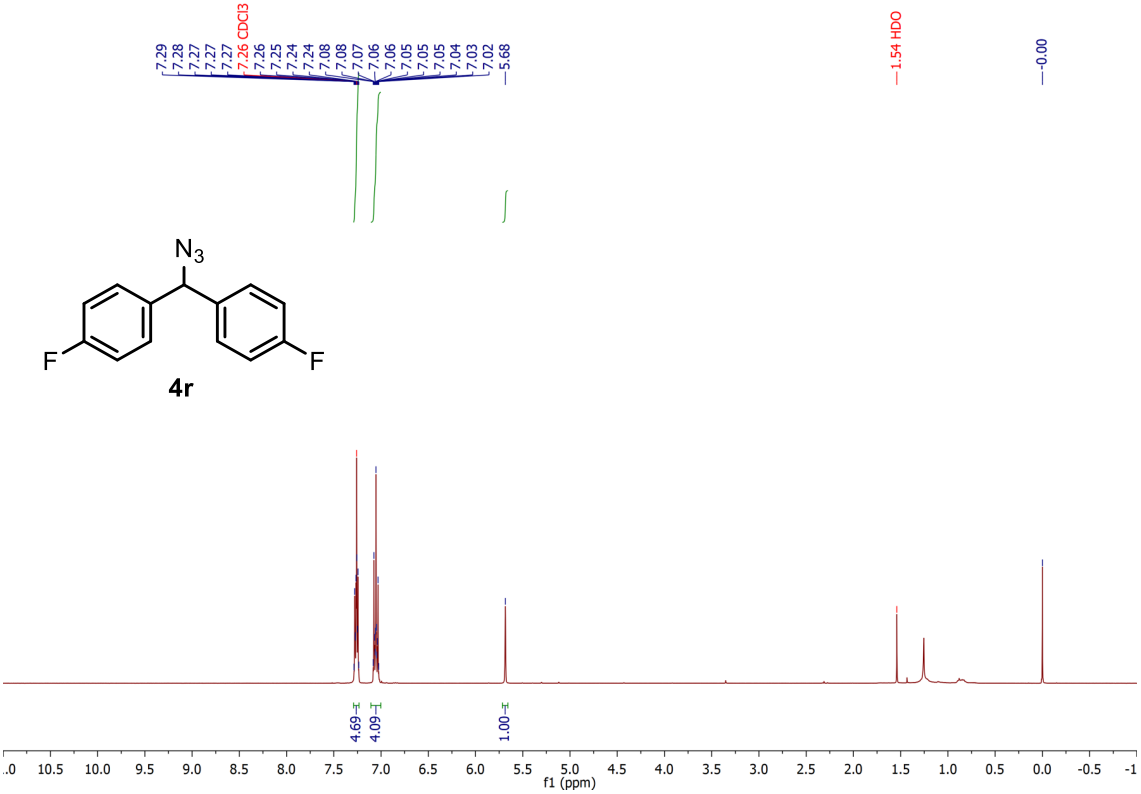
^{13}C NMR spectrum of **4p** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



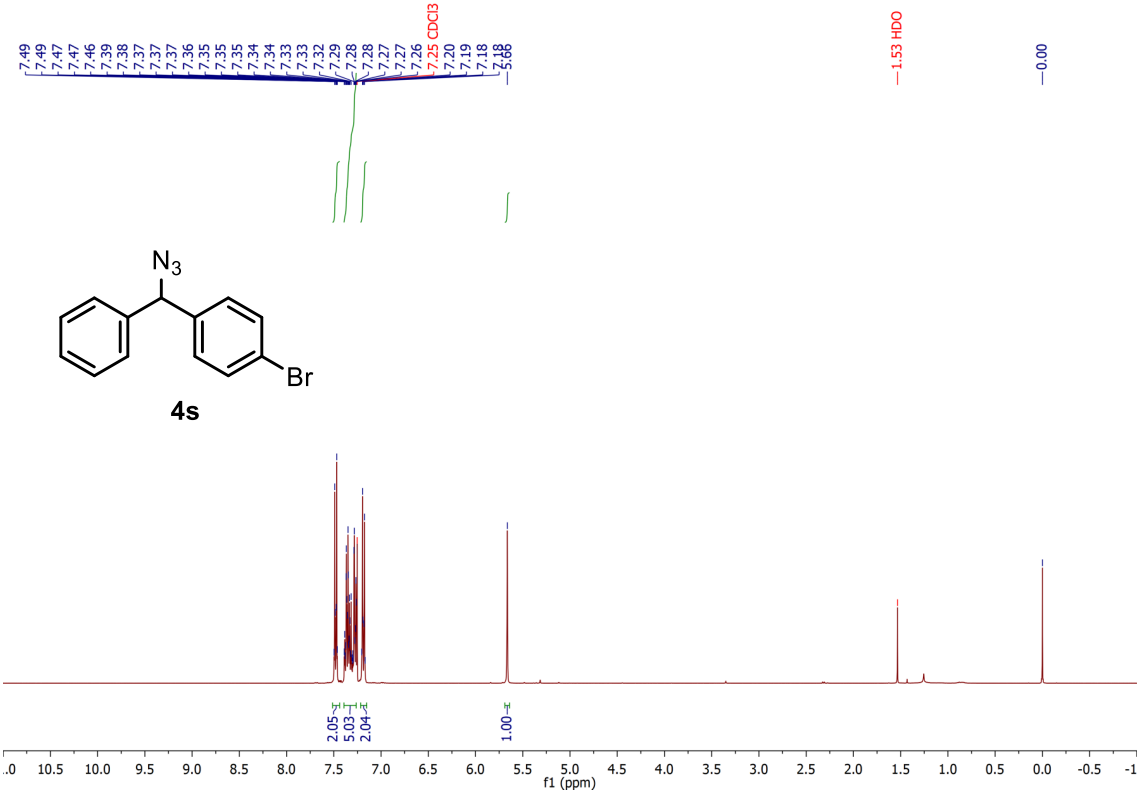
^{1}H NMR spectrum of **4q** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



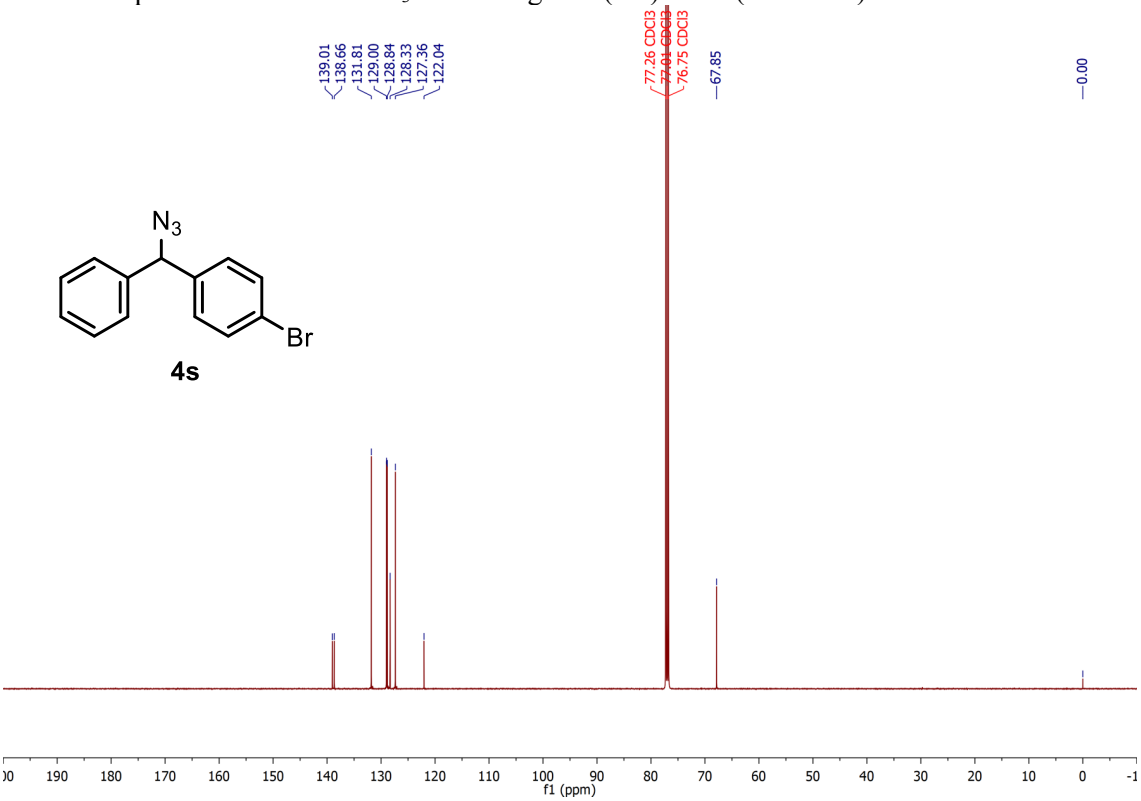
^{1}H NMR spectrum of **4r** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



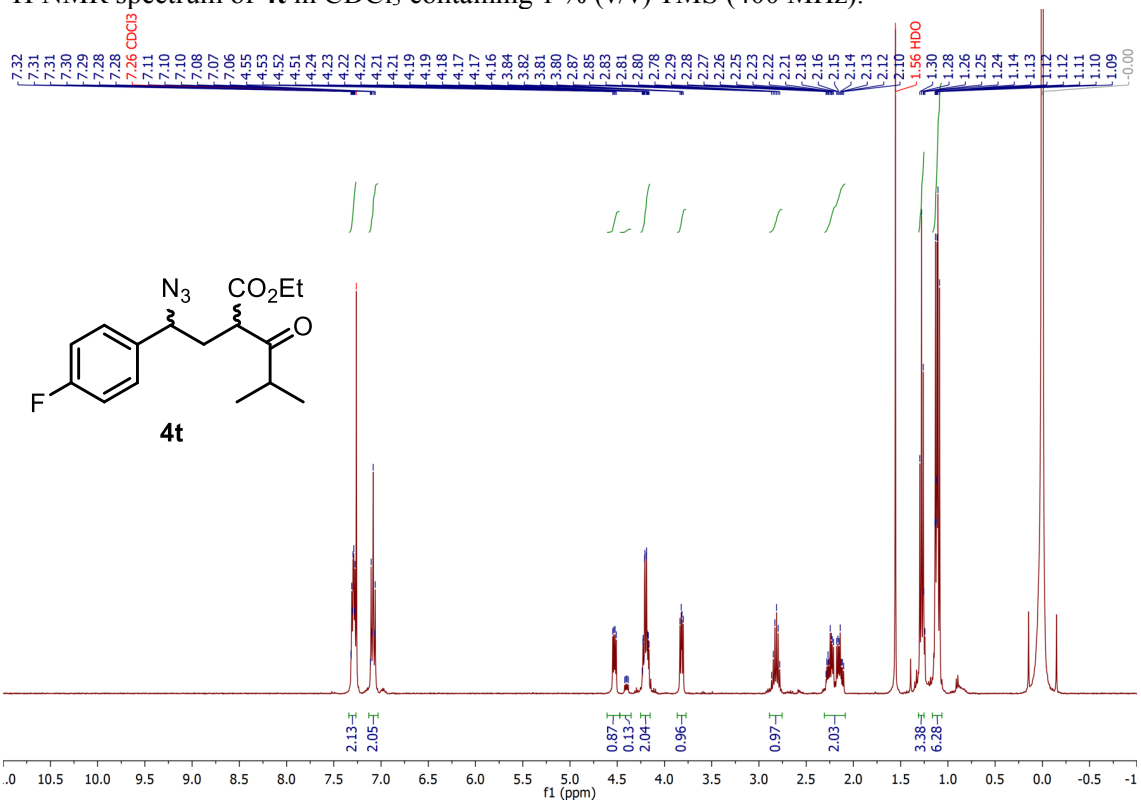
^{1}H NMR spectrum of **4s** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



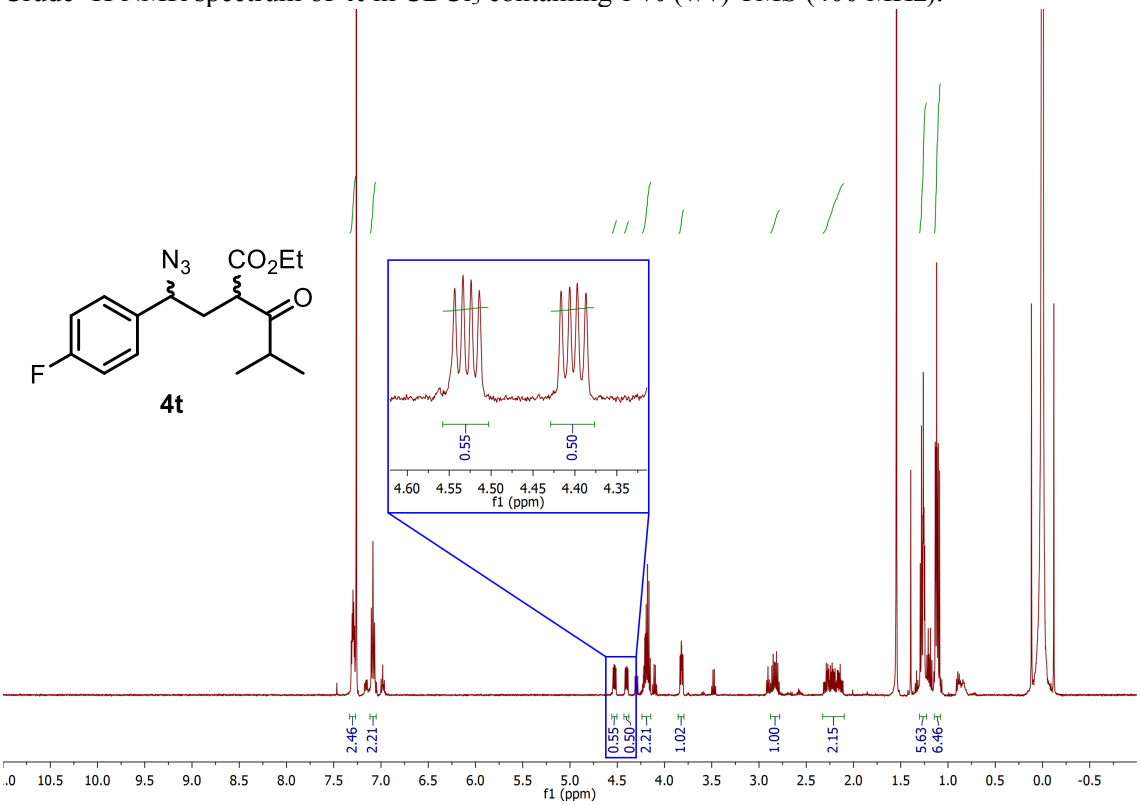
^{13}C NMR spectrum of **4s** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



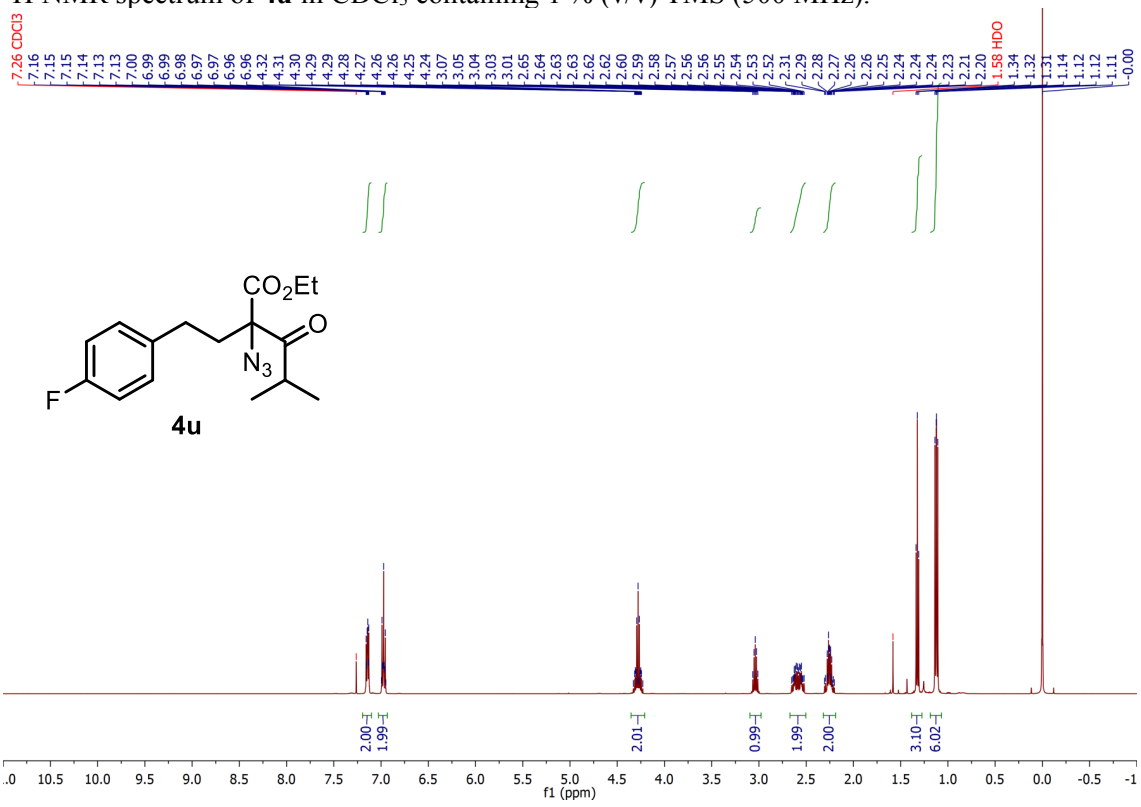
^{1}H NMR spectrum of **4t** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



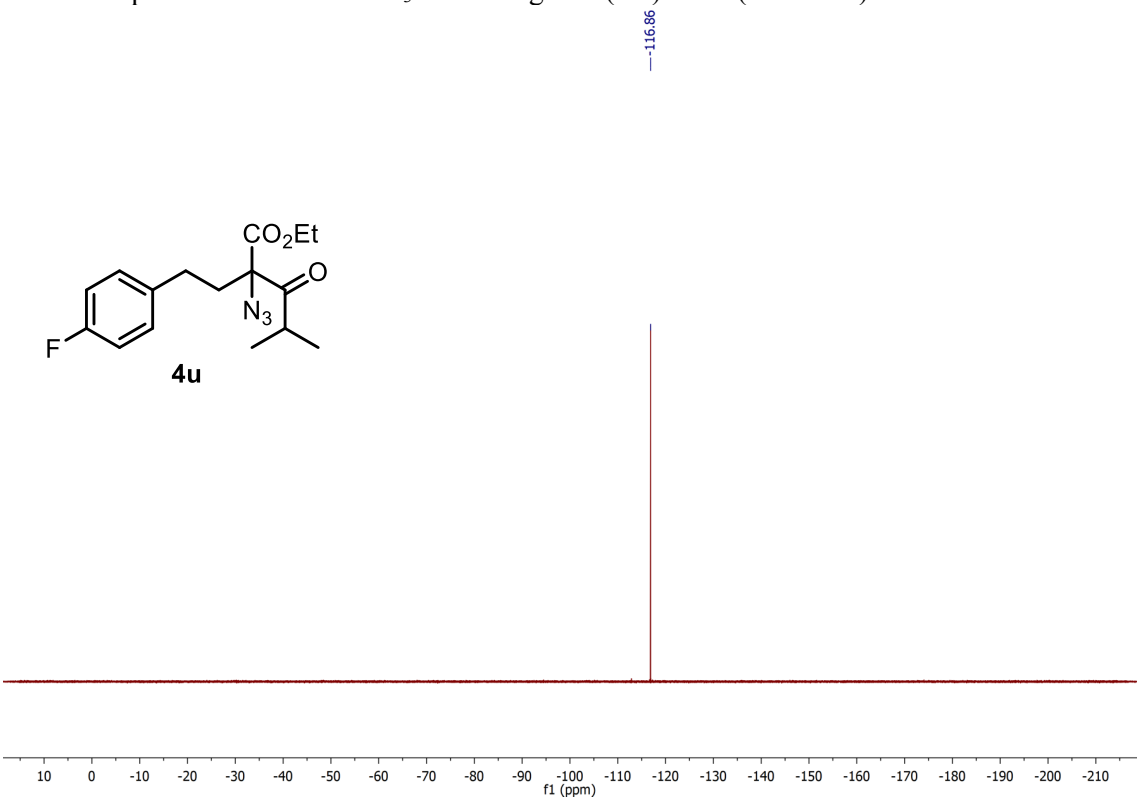
Crude ^{1}H NMR spectrum of **4t** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



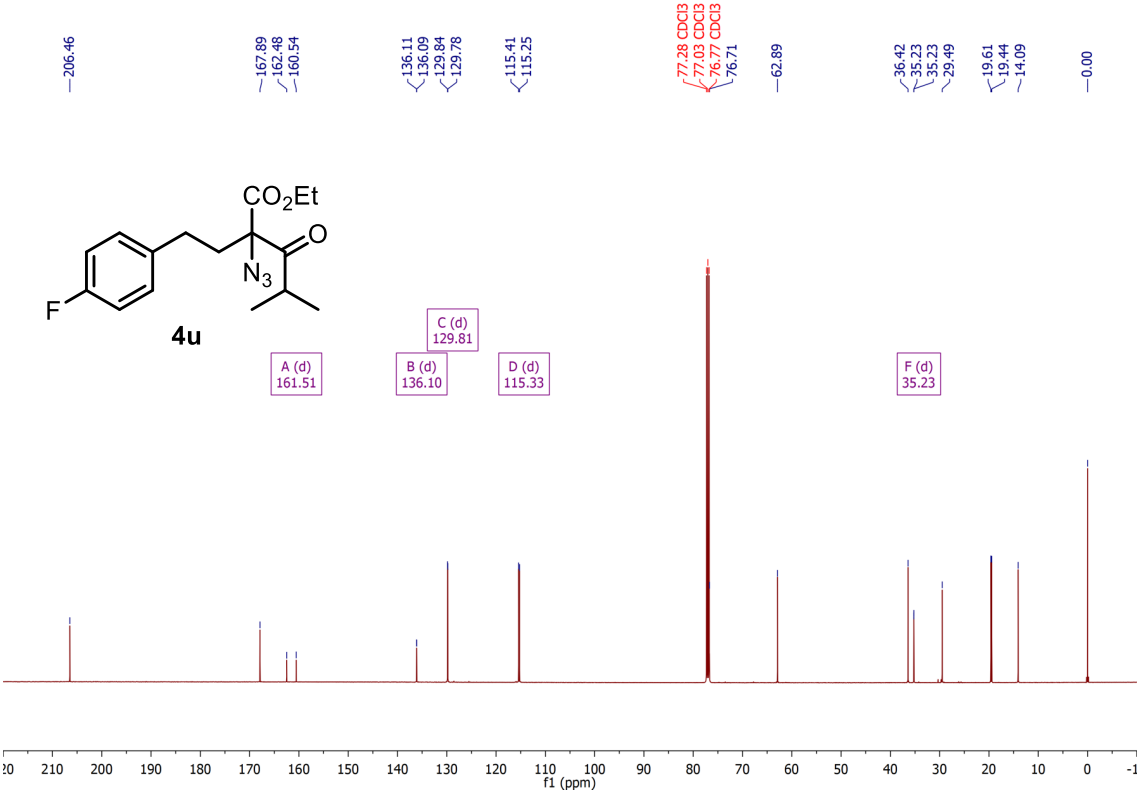
^{1}H NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



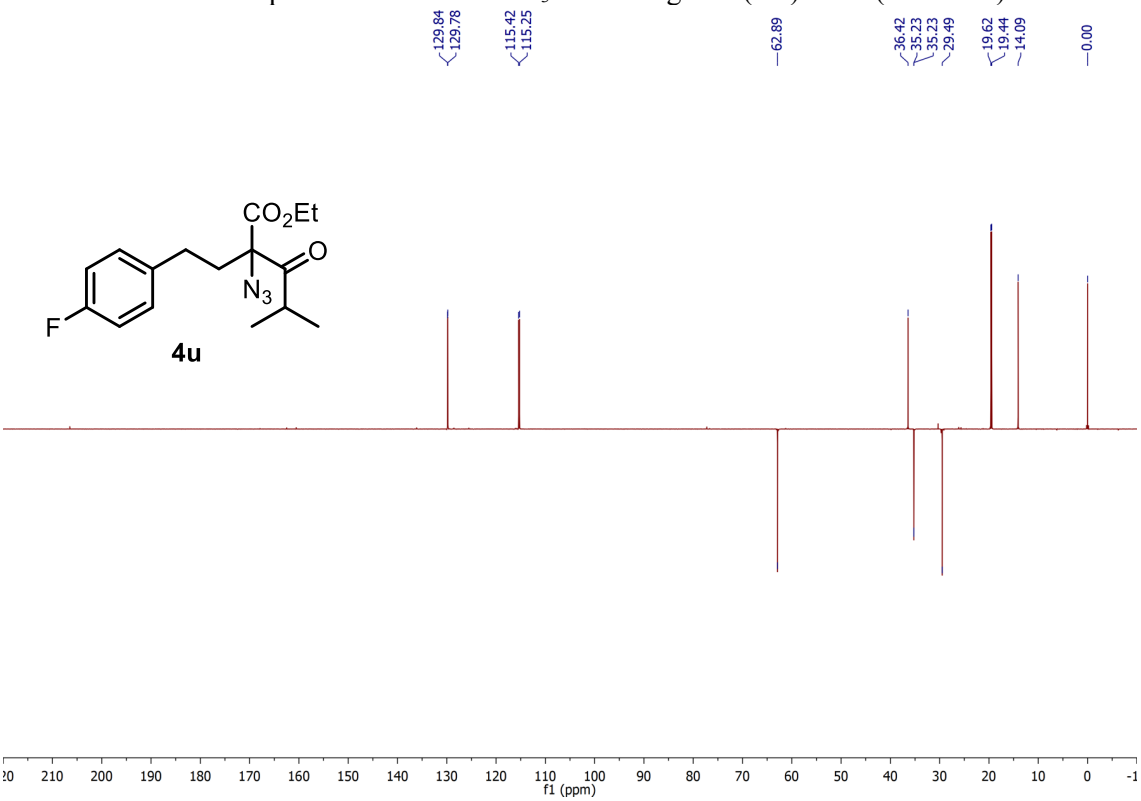
^{19}F NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



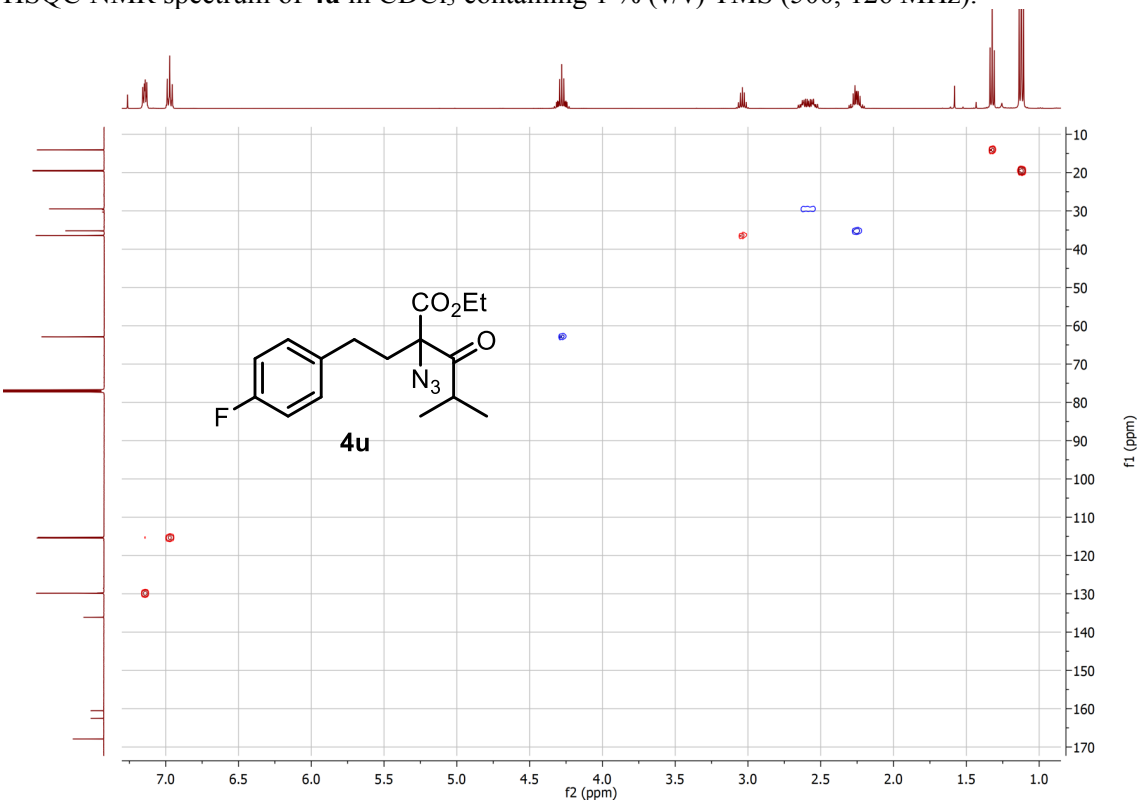
^{13}C NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



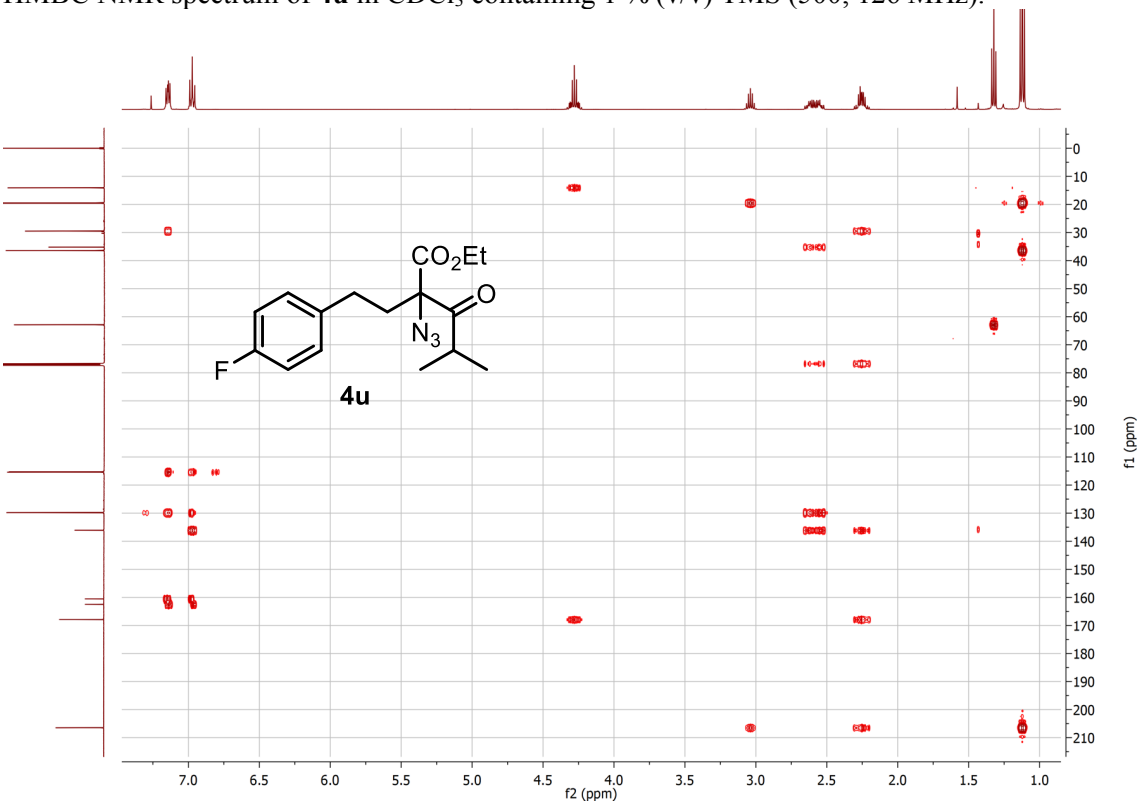
^{13}C DEPT-135 NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



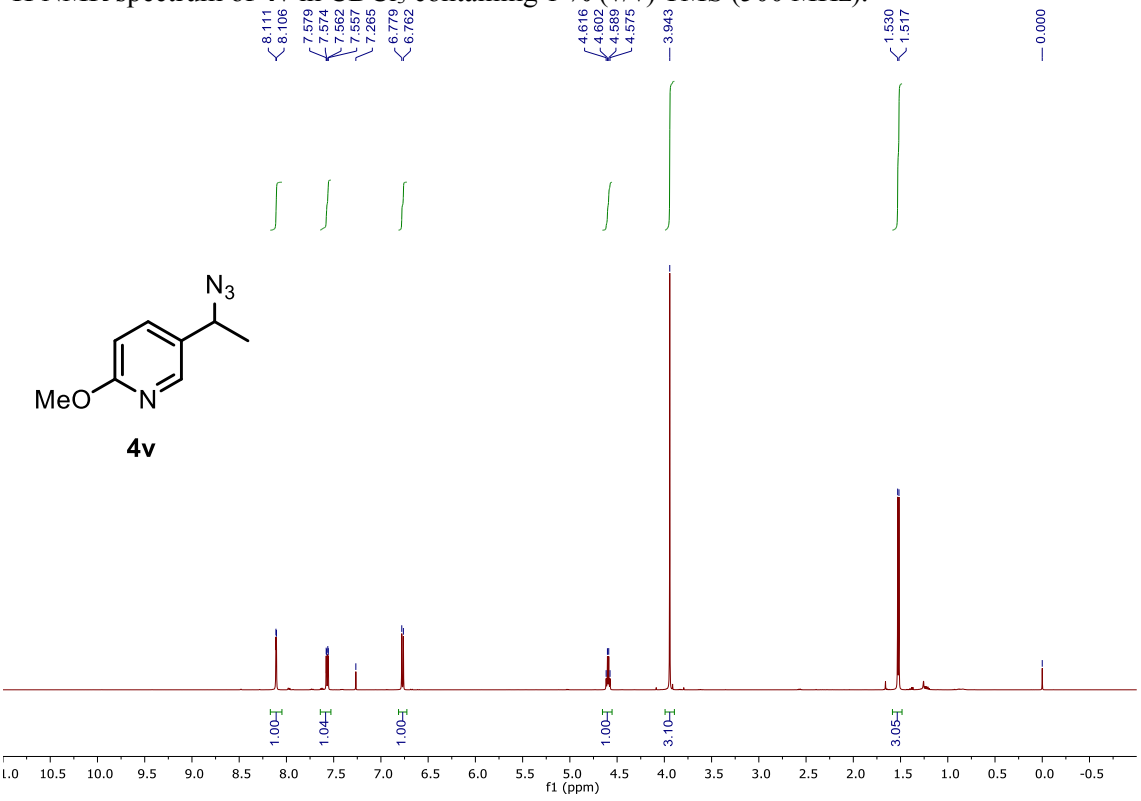
HSQC NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



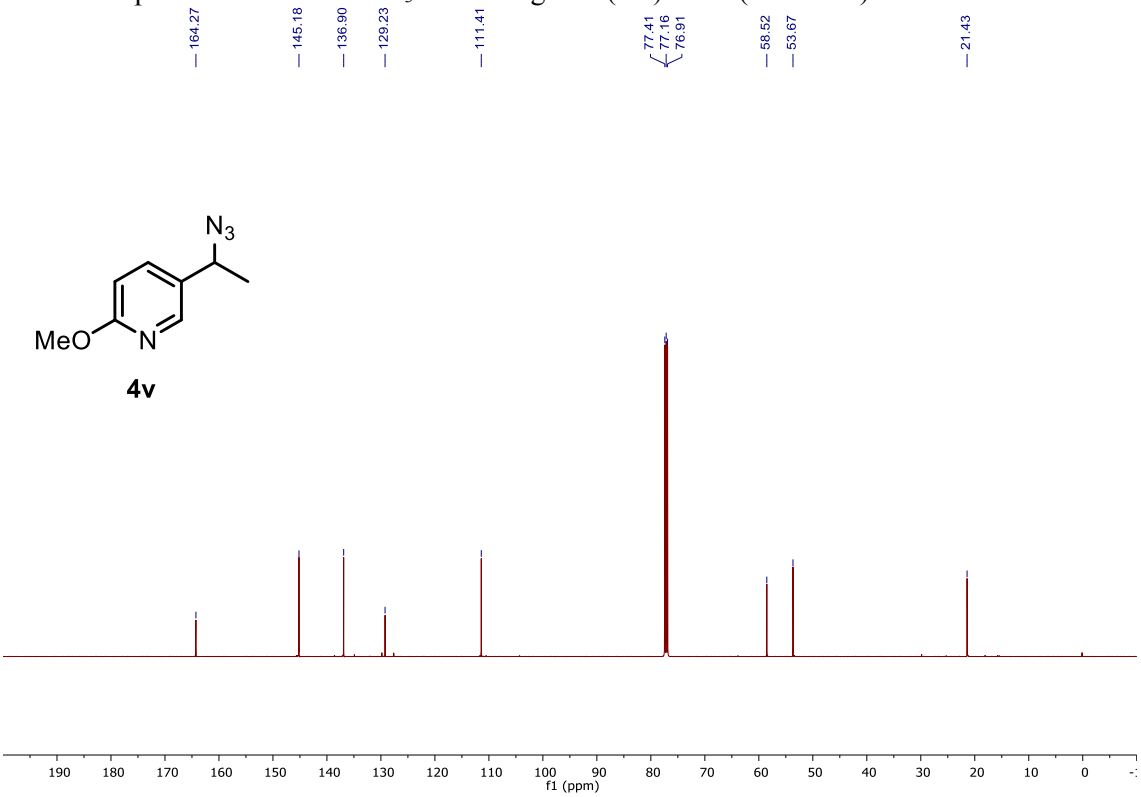
HMBC NMR spectrum of **4u** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



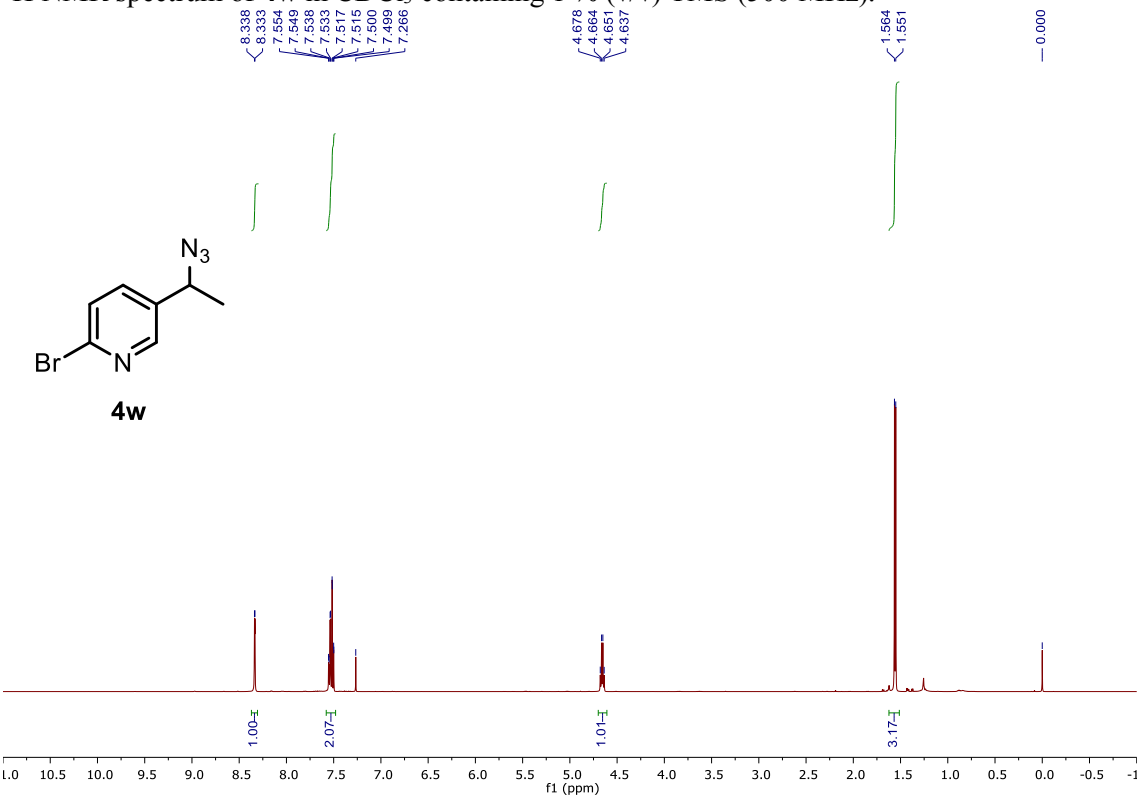
^{1}H NMR spectrum of **4v** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



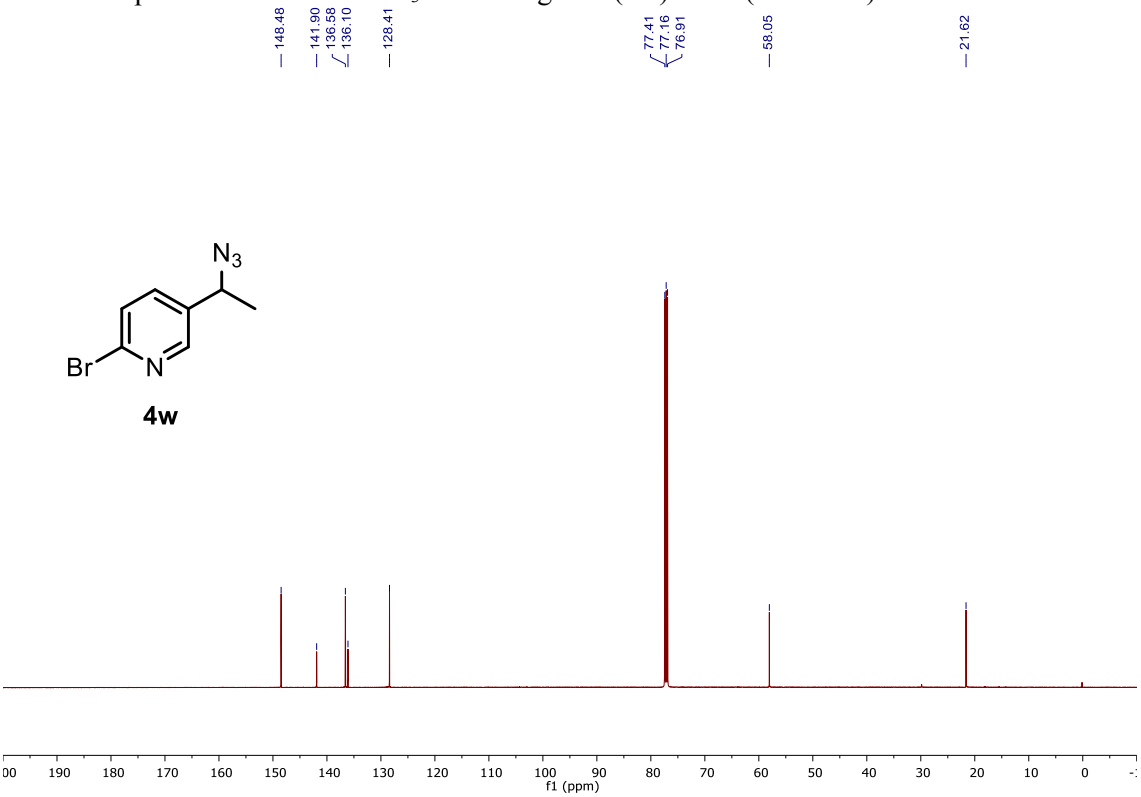
^{13}C NMR spectrum of **4v** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



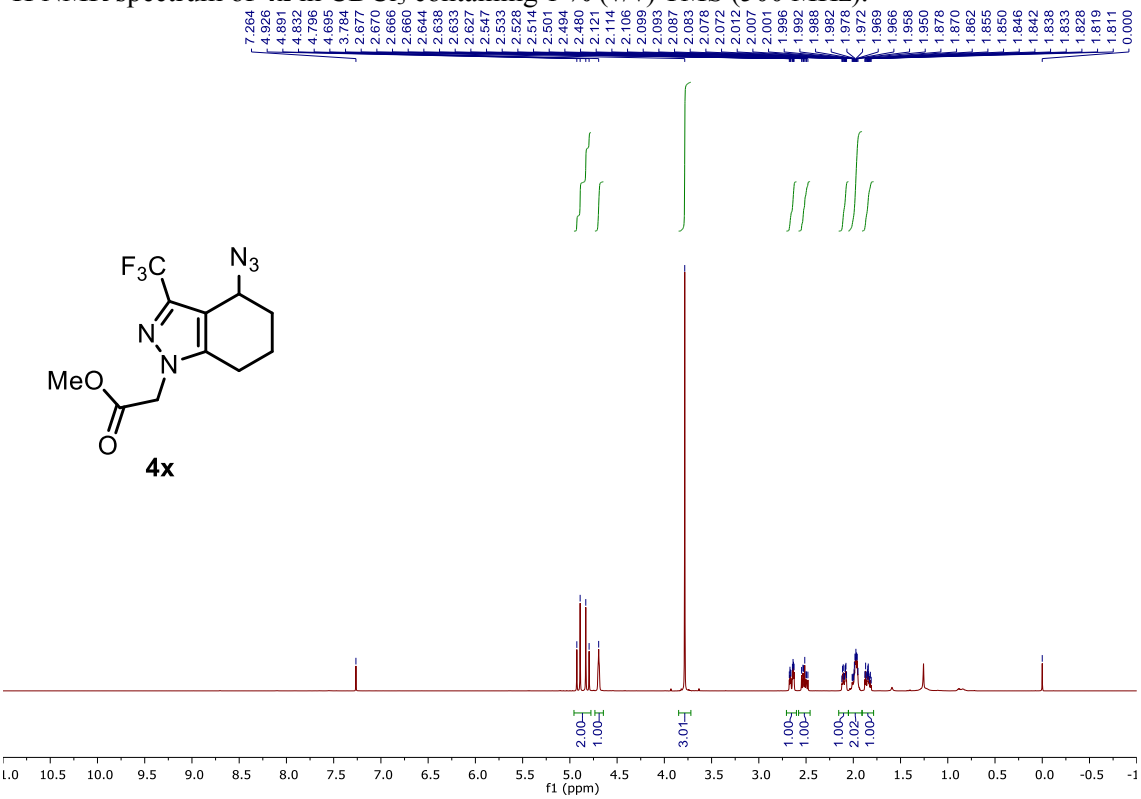
^{1}H NMR spectrum of **4w** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



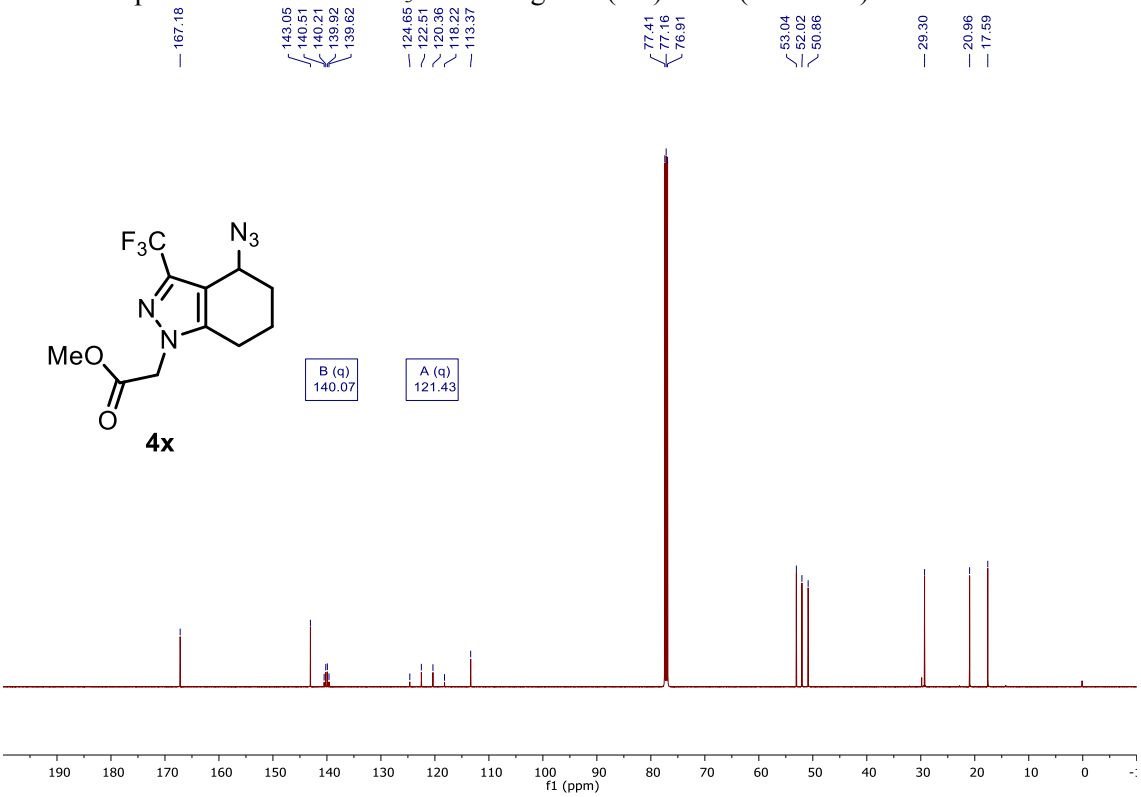
^{13}C NMR spectrum of **4w** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



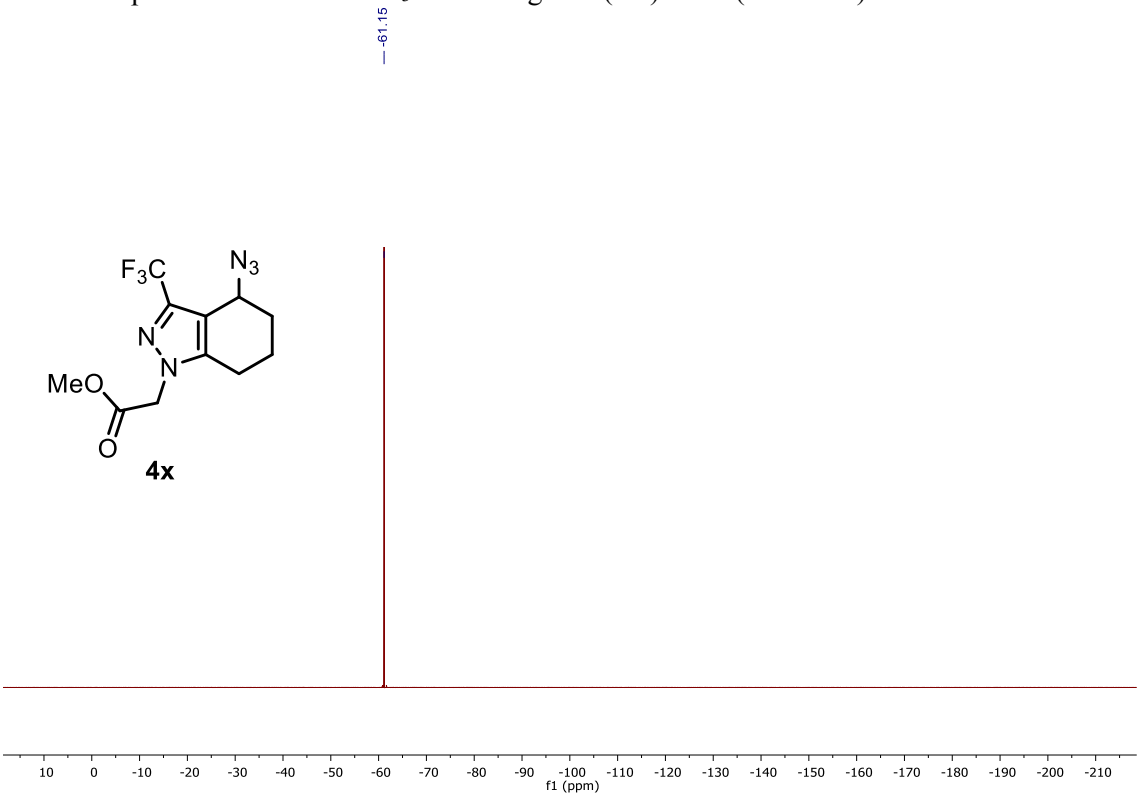
^{1}H NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



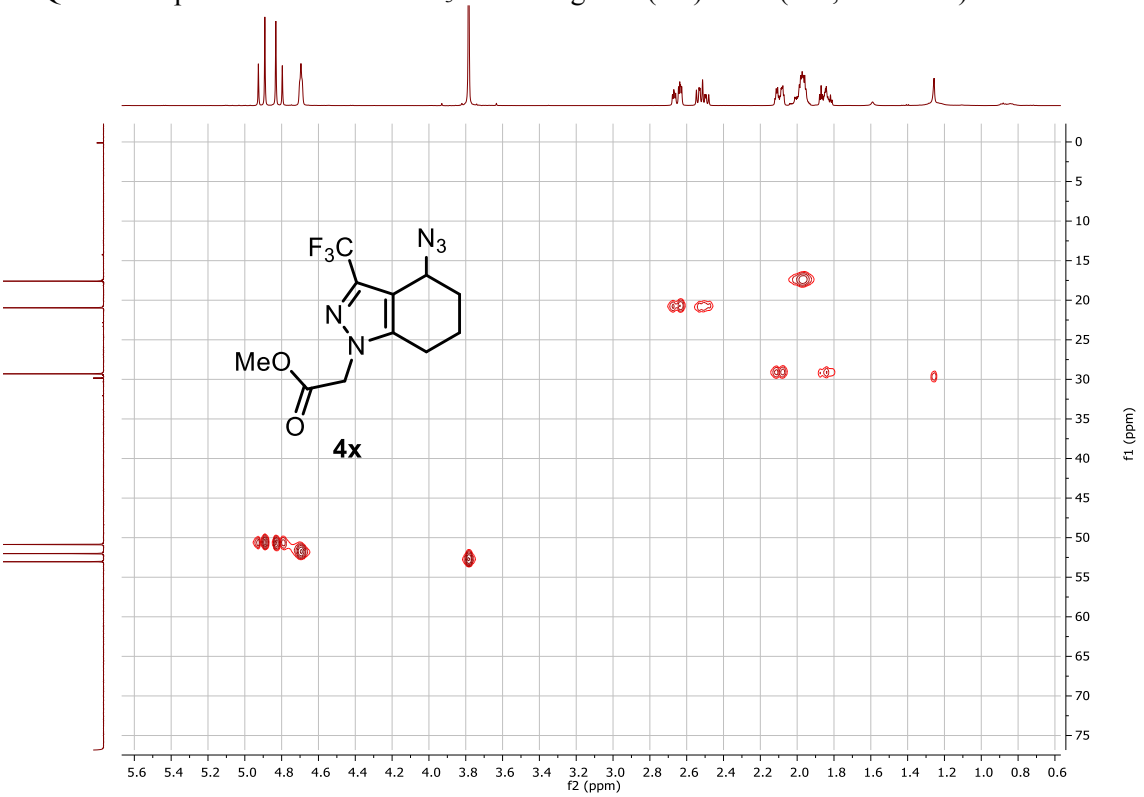
^{13}C NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



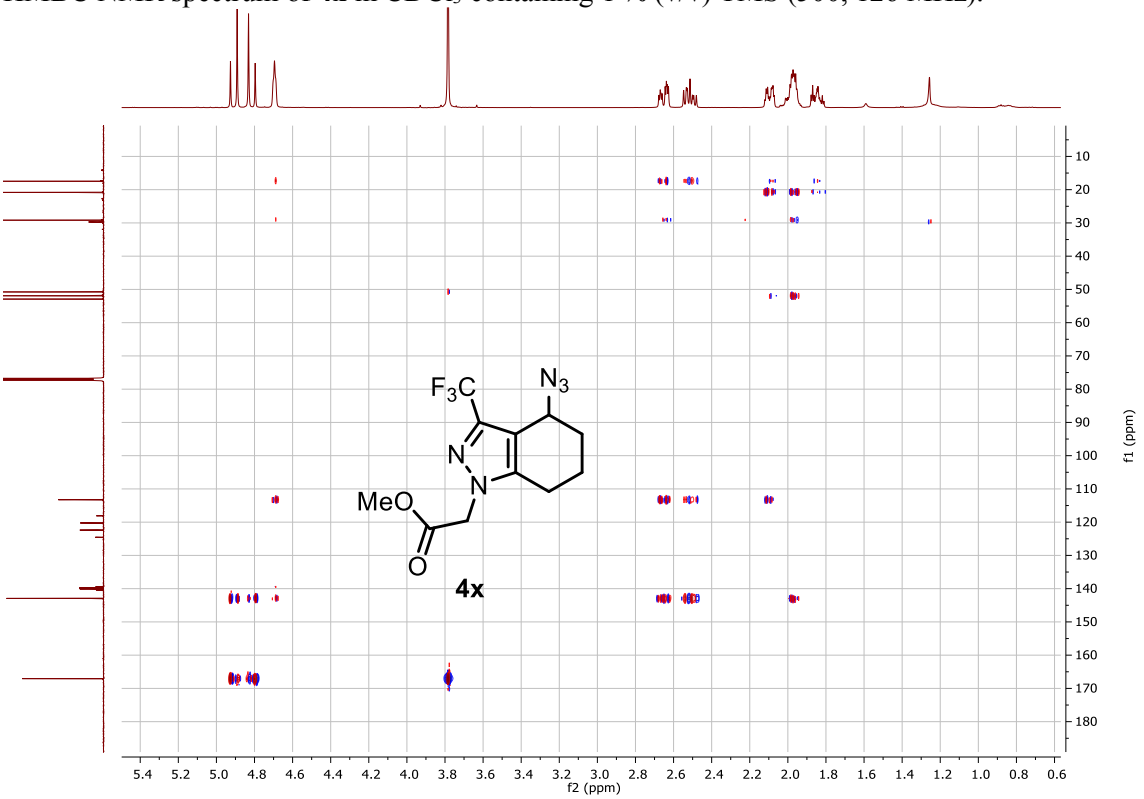
^{19}F NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



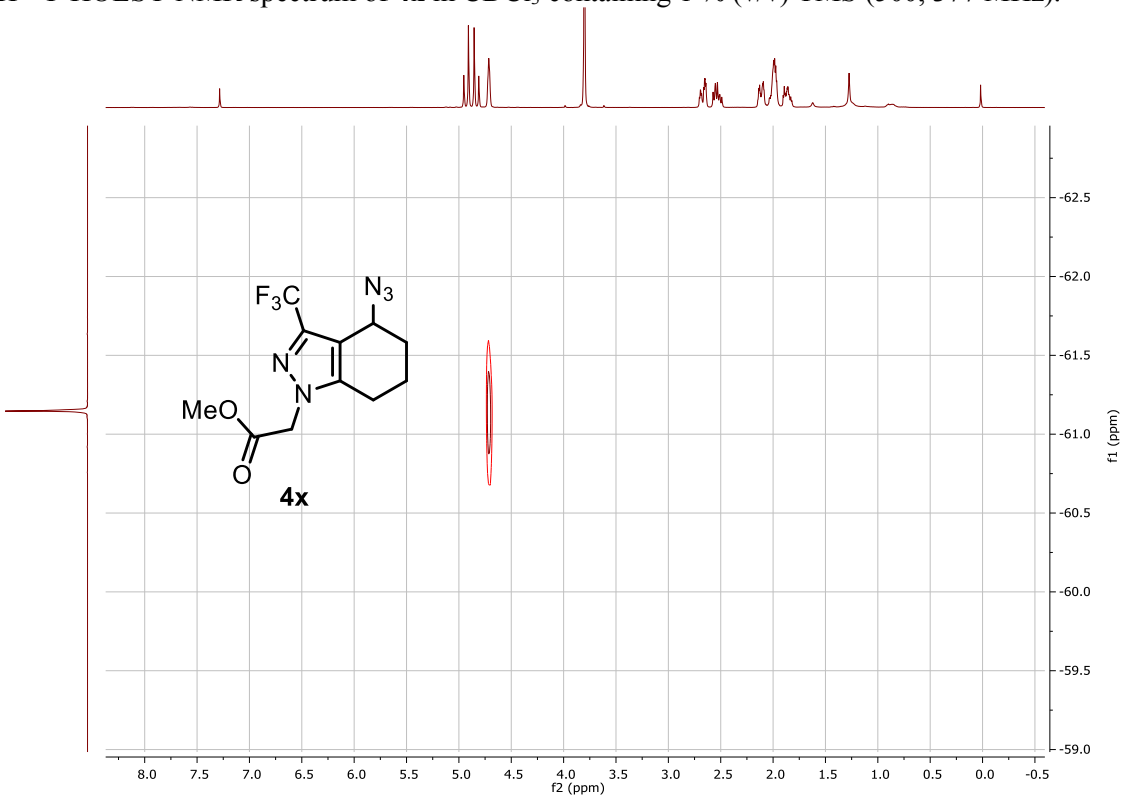
HSQC NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



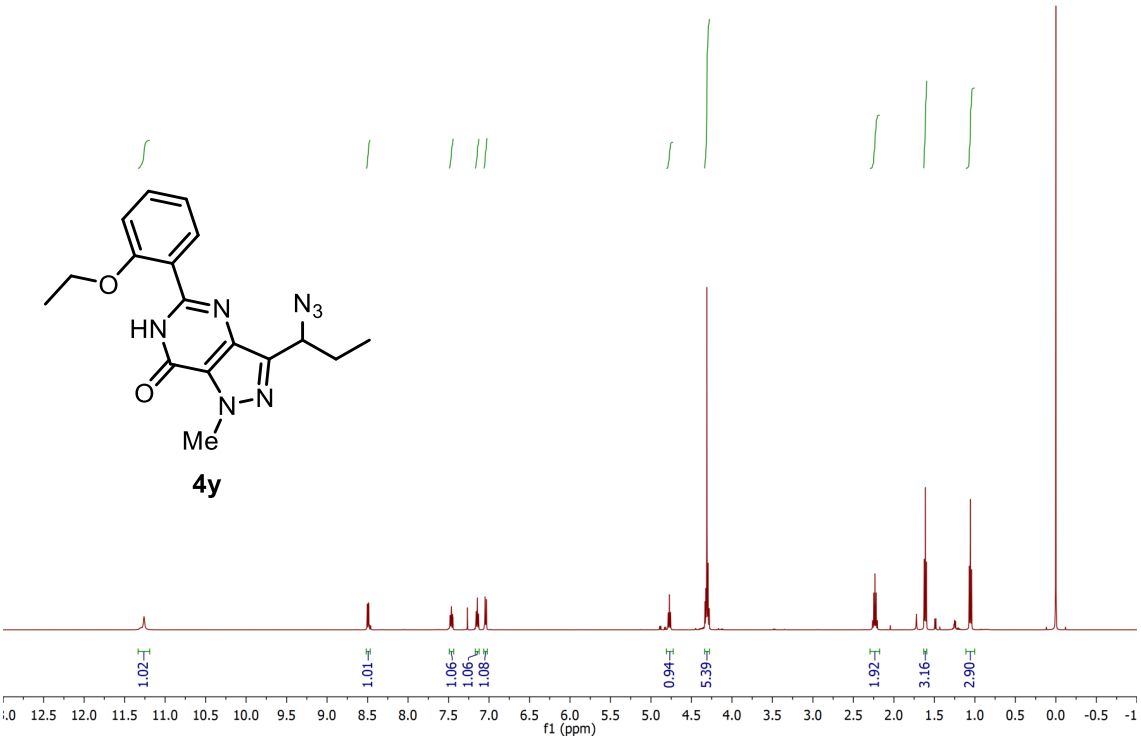
HMBC NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



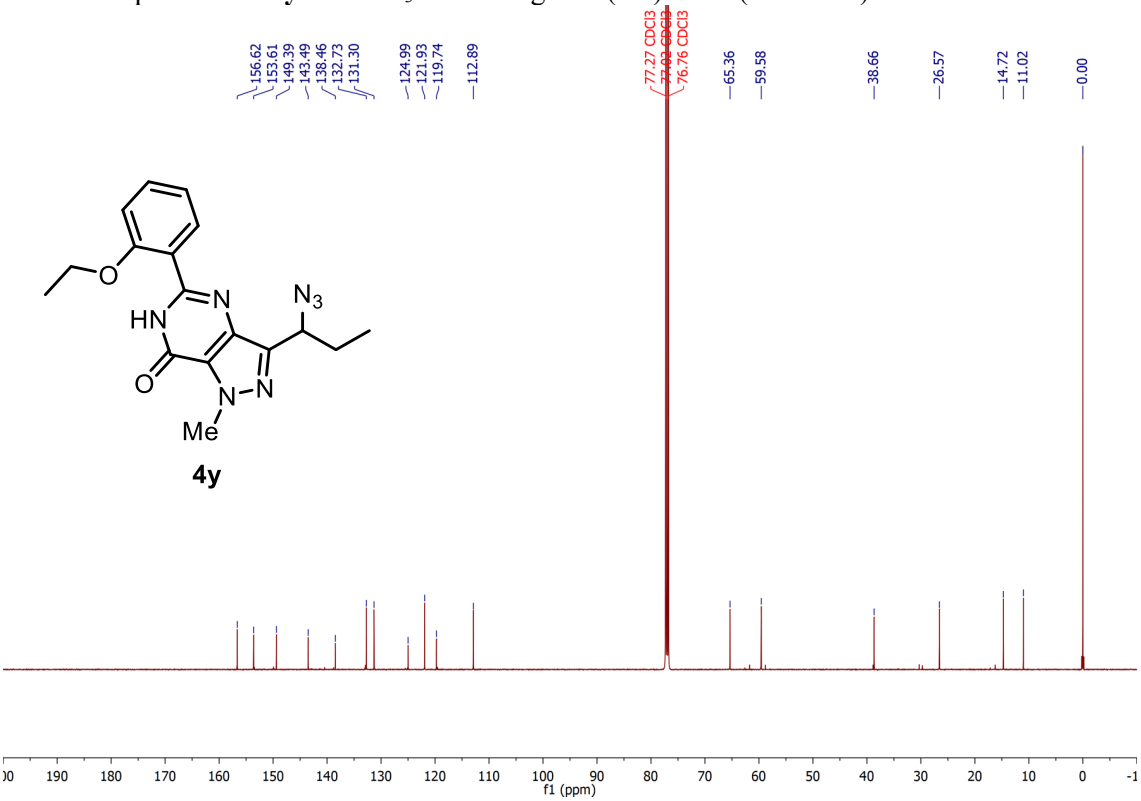
^{1}H-^{19}F HOESY NMR spectrum of **4x** in $CDCl_3$ containing 1 % (v/v) TMS (500, 377 MHz).



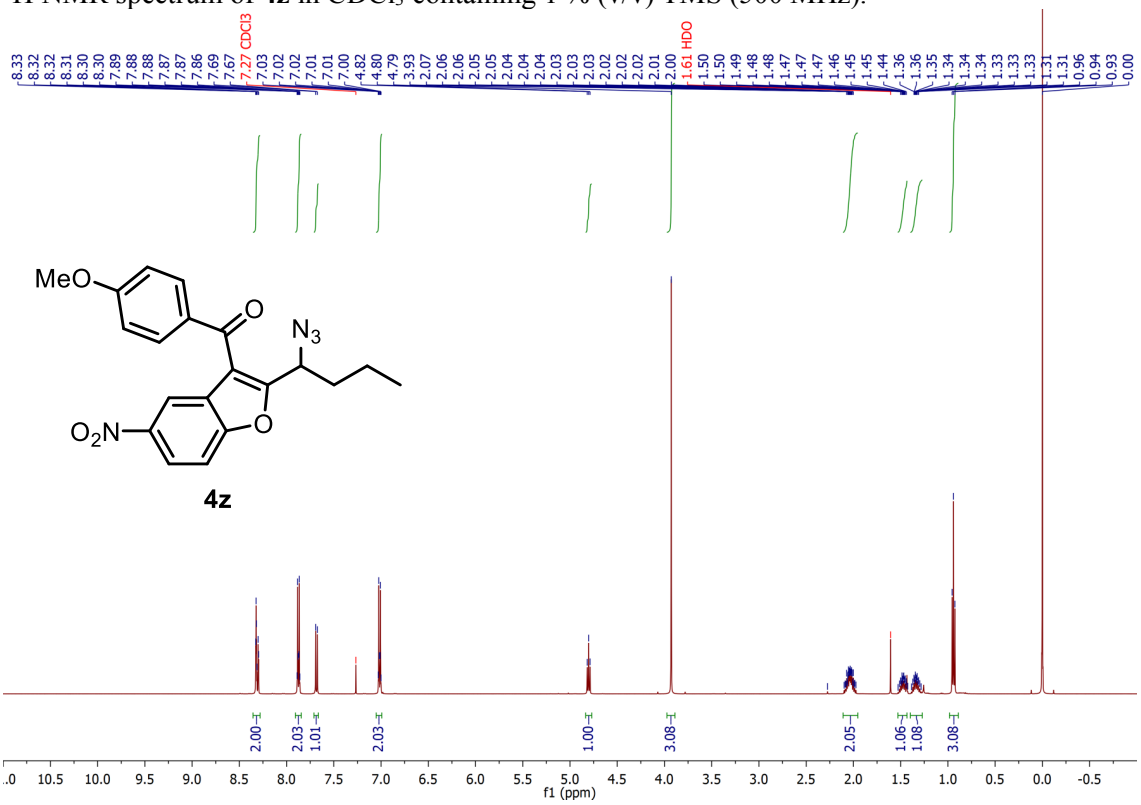
^{1}H NMR spectrum of **4y** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



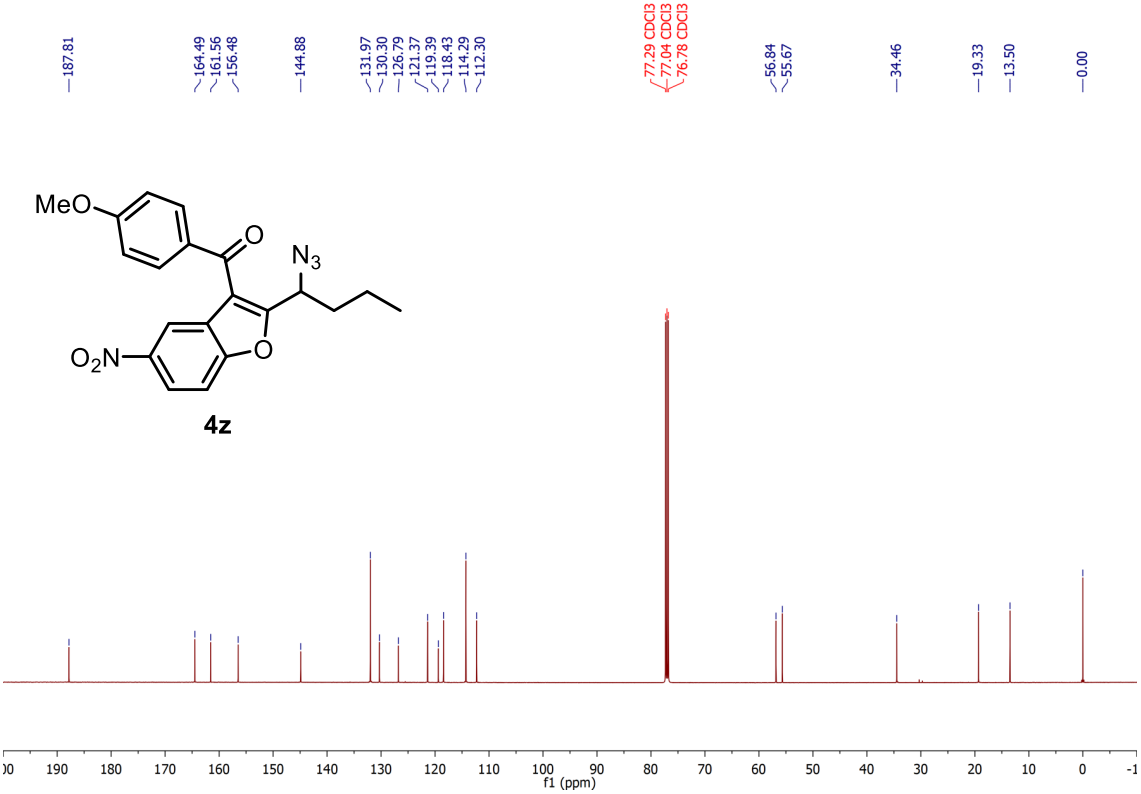
^{13}C NMR spectrum of **4y** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



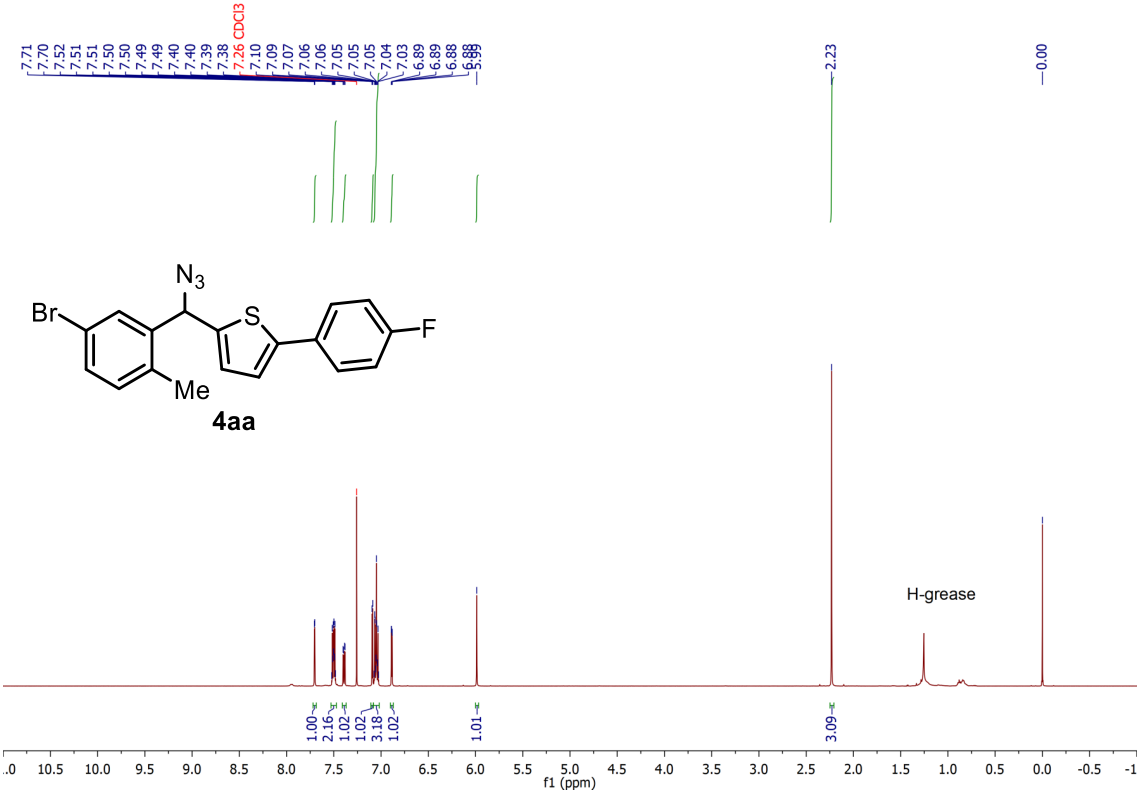
^{1}H NMR spectrum of **4z** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



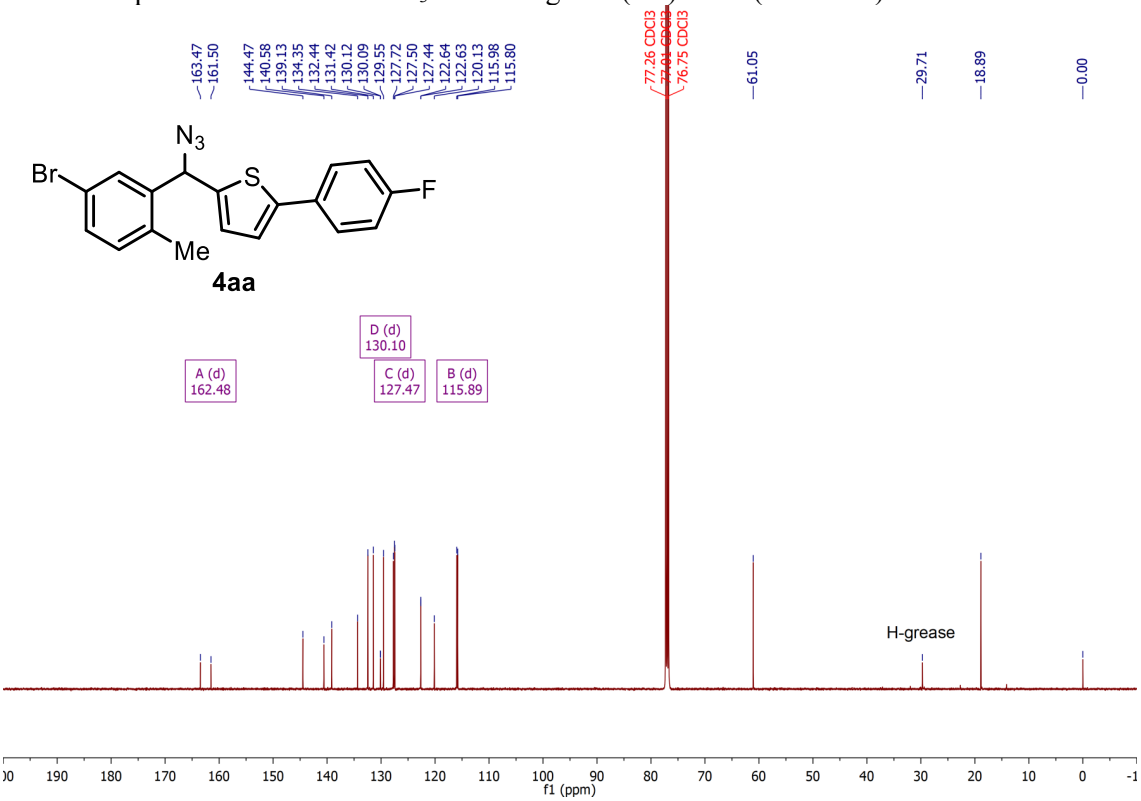
^{13}C NMR spectrum of **4z** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



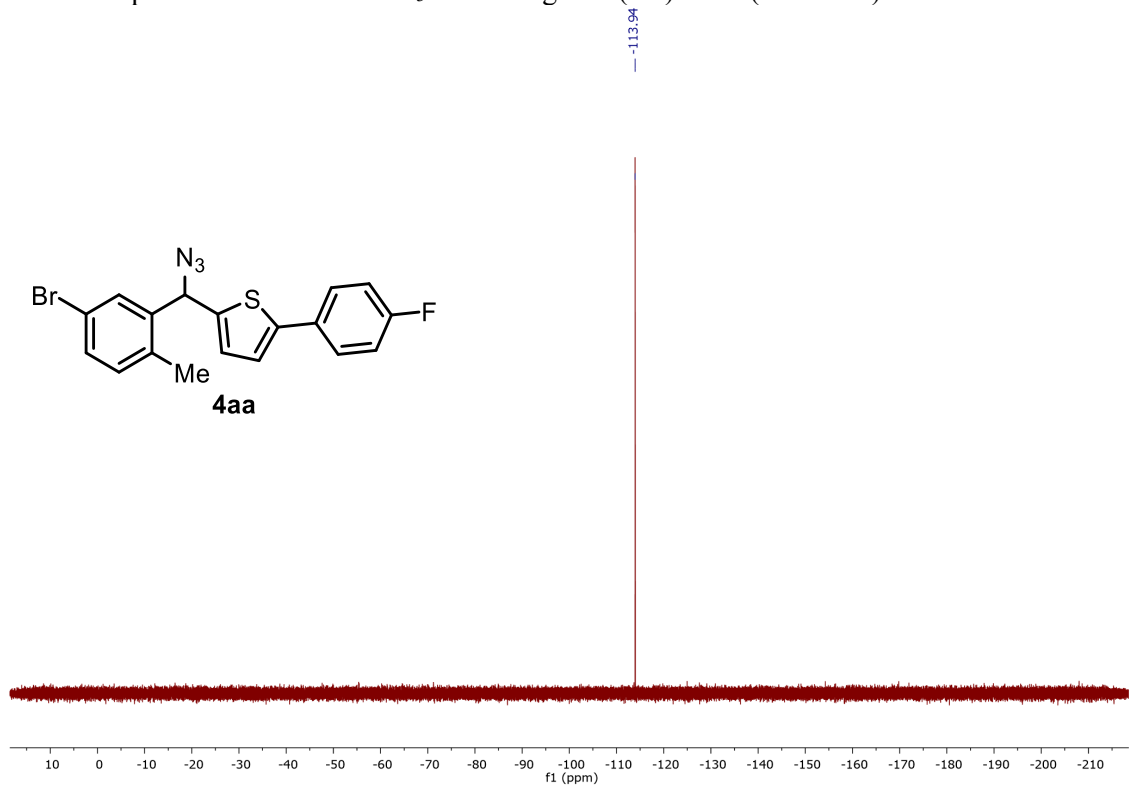
^{1}H NMR spectrum of **4aa** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



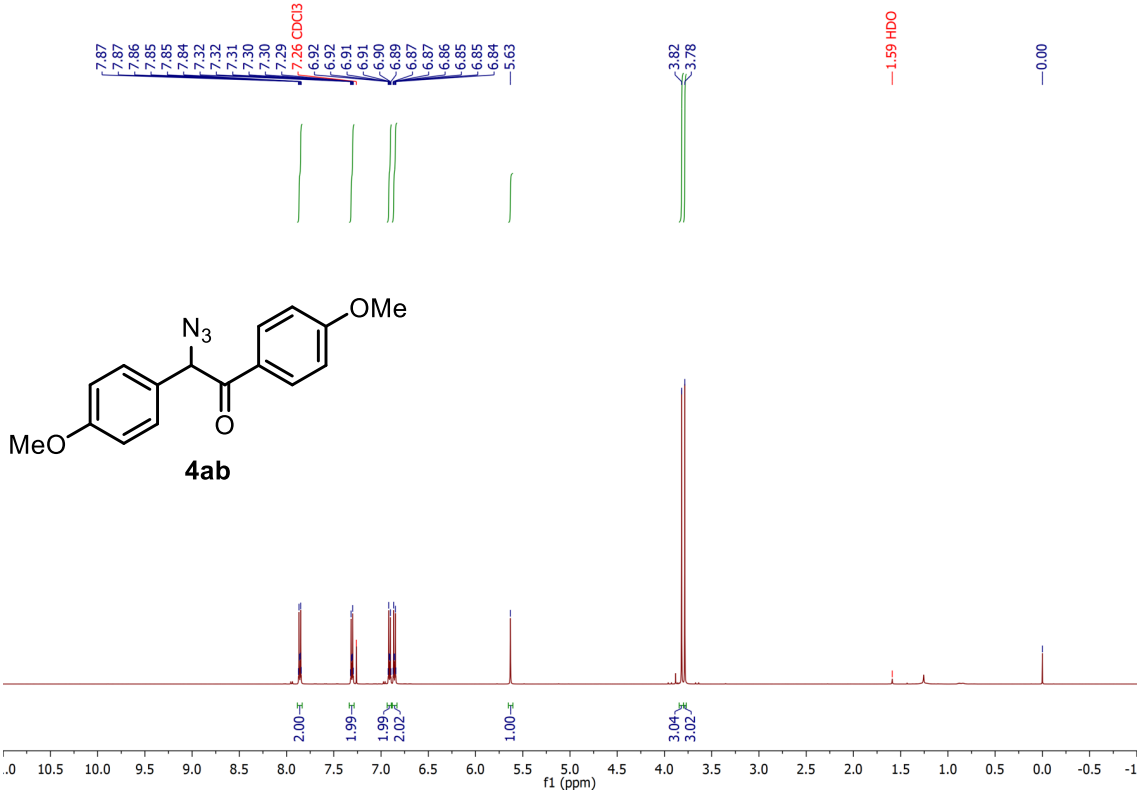
^{13}C NMR spectrum of **4aa** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



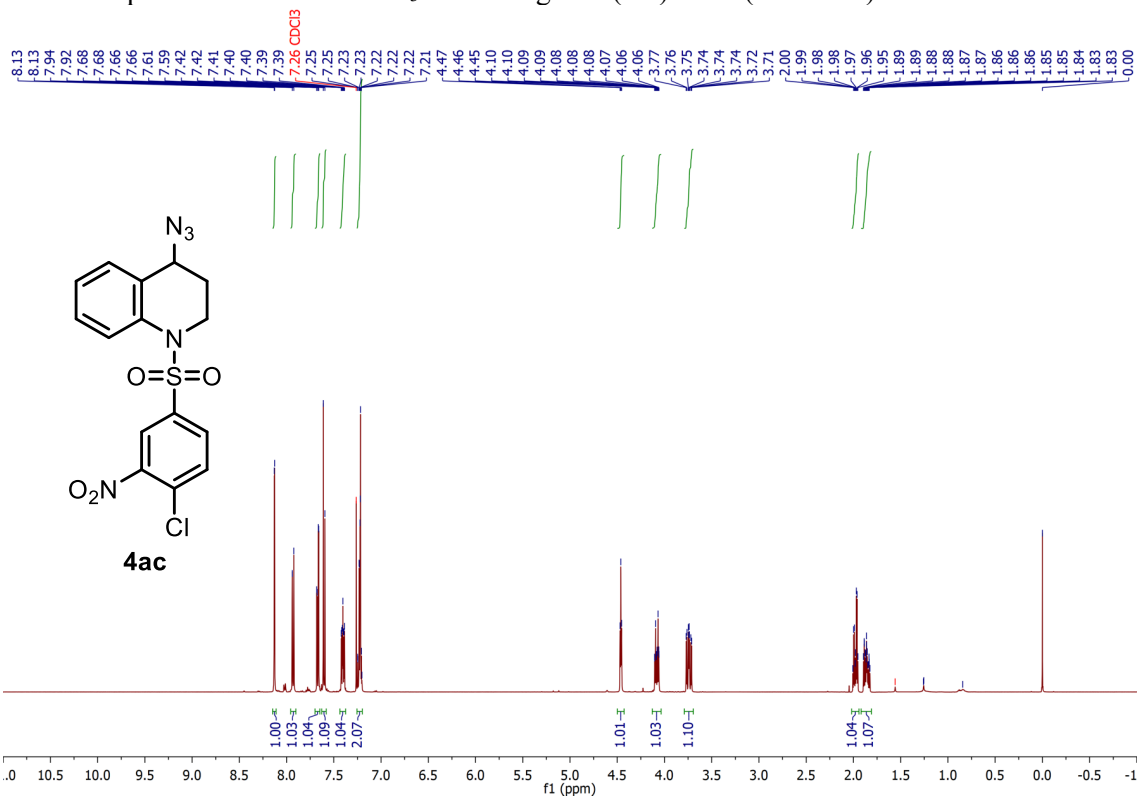
^{19}F NMR spectrum of **4aa** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



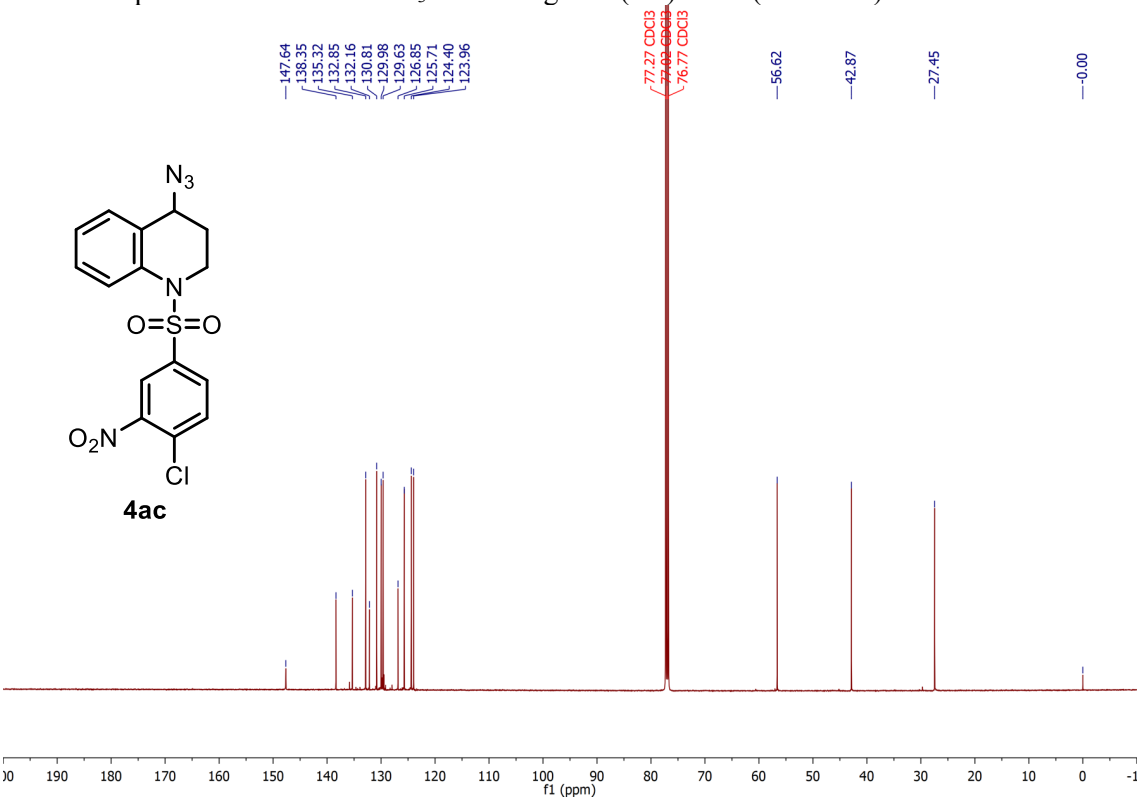
^{1}H NMR spectrum of **4ab** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



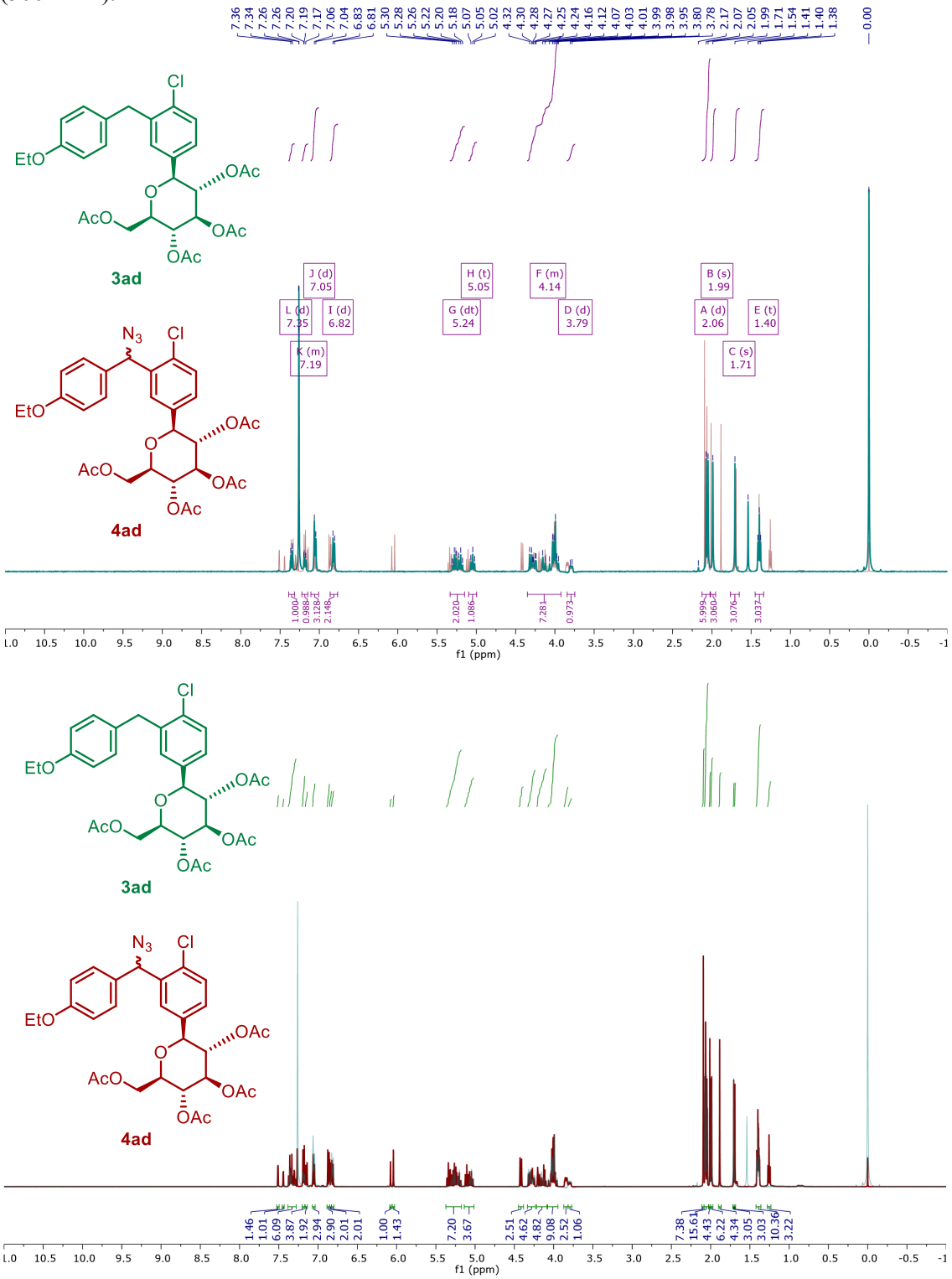
^{1}H NMR spectrum of **4ac** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



^{13}C NMR spectrum of **4ac** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).

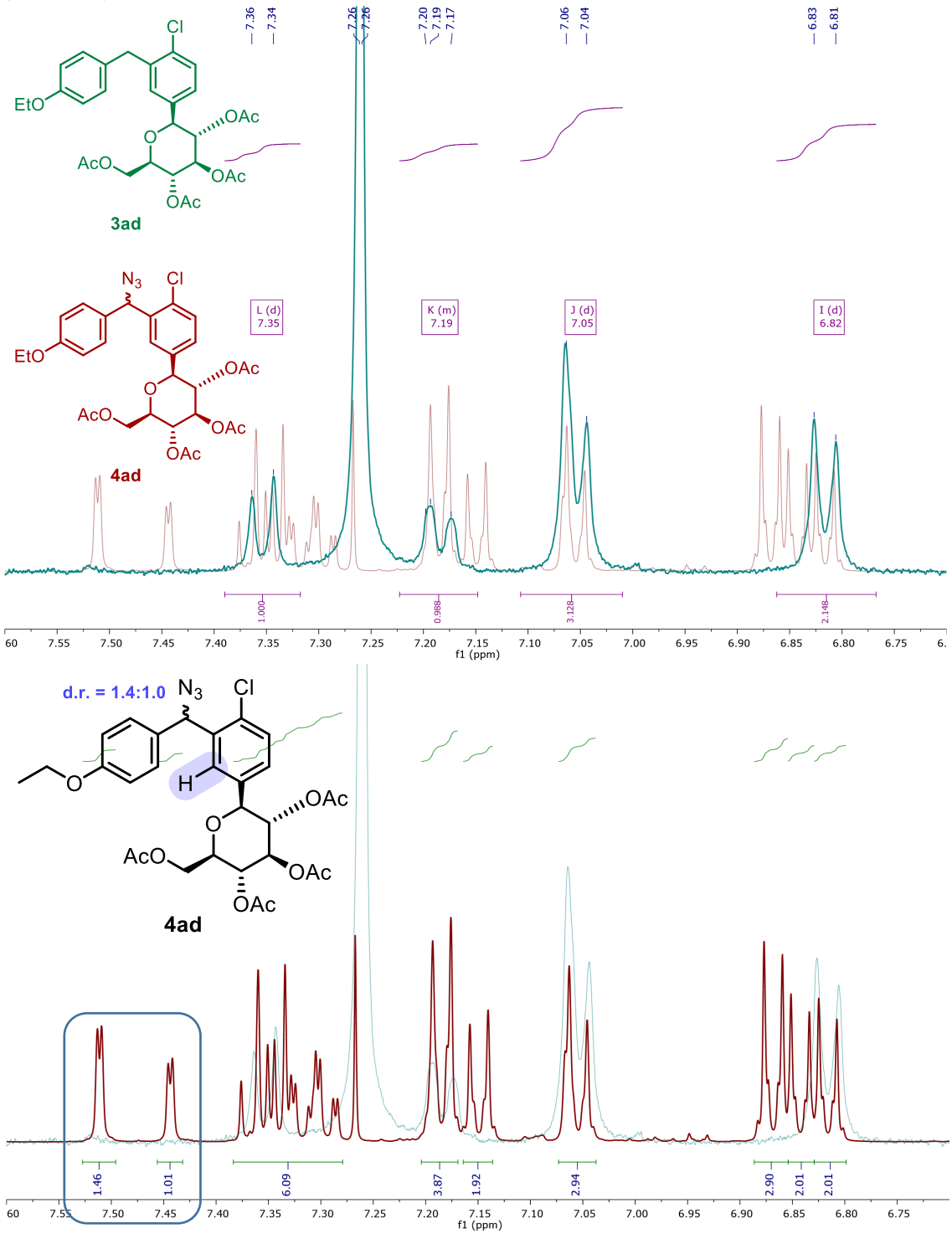


Superimposed ^{1}H NMR spectra of **3ad** and a mixture of **3ad** and **4ad** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



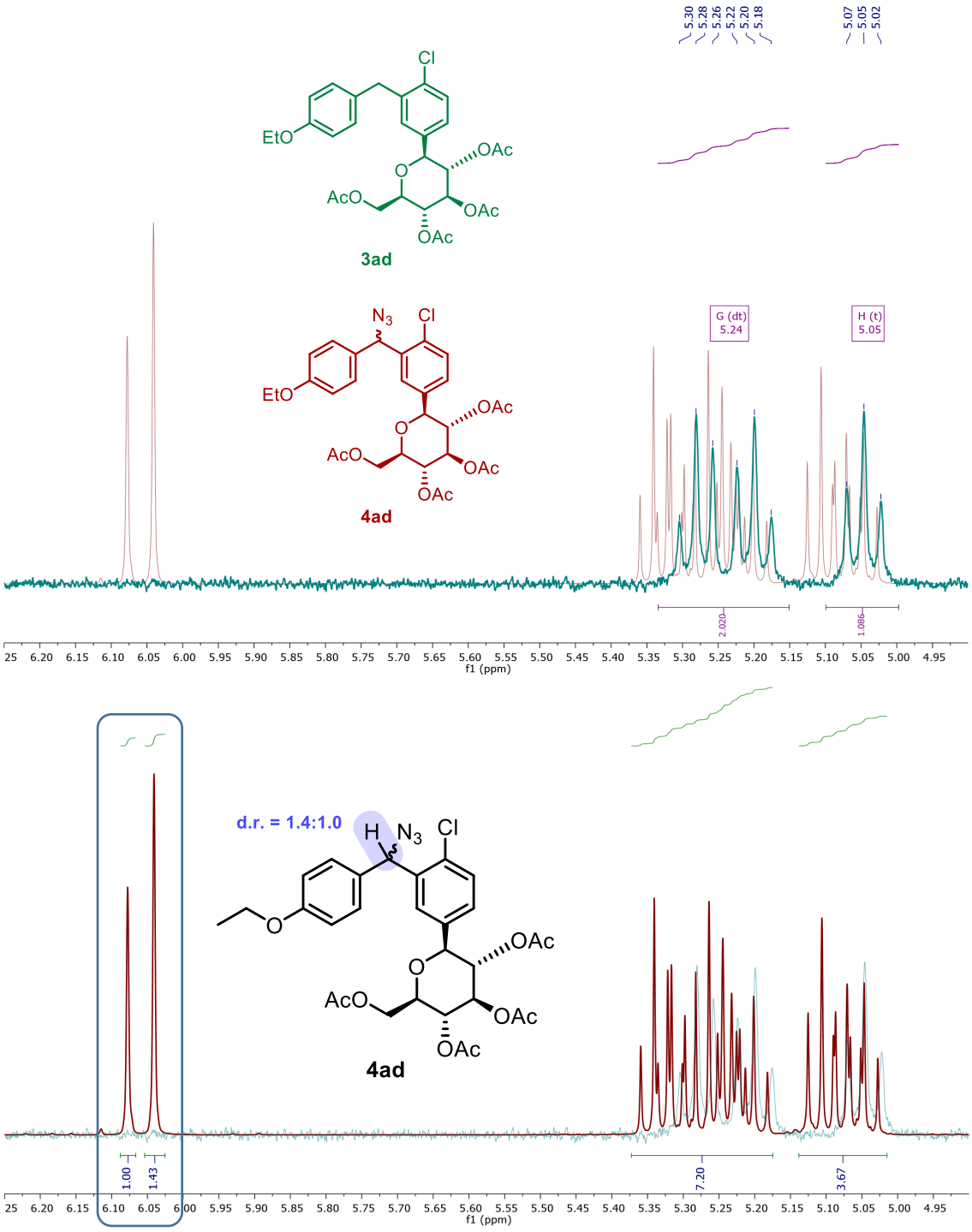
* **Green-** and **red-** colored peaks represent **3ad** and **a mixture of 3ad and 4ad** respectively.

Superimposed ^{1}H NMR spectra of **3ad** and a mixture of **3ad** and **4ad** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



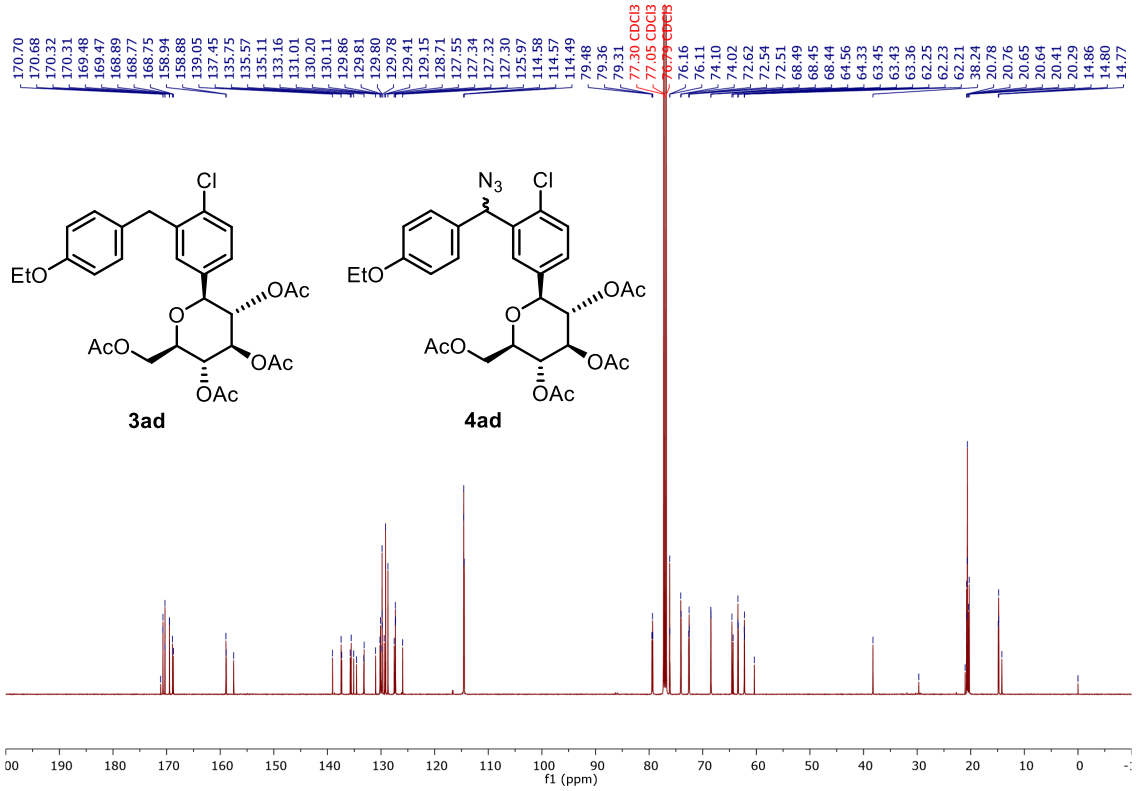
* **Green-** and **red-** colored peaks represent **3ad** and **a mixture of 3ad and 4ad** respectively.

Superimposed ^{1}H NMR spectra of **3ad** and a mixture of **3ad** and **4ad** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).

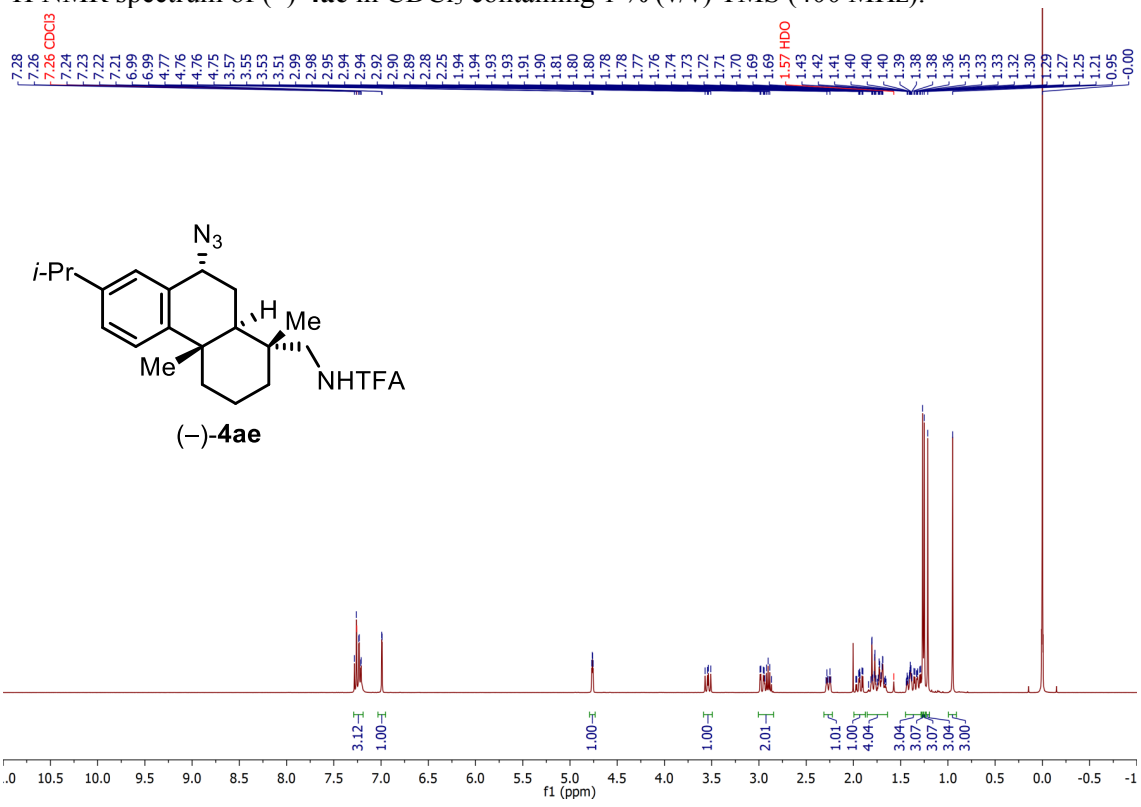


* **Green-** and **red-** colored peaks represent **3ad** and **a mixture of 3ad and 4ad** respectively.

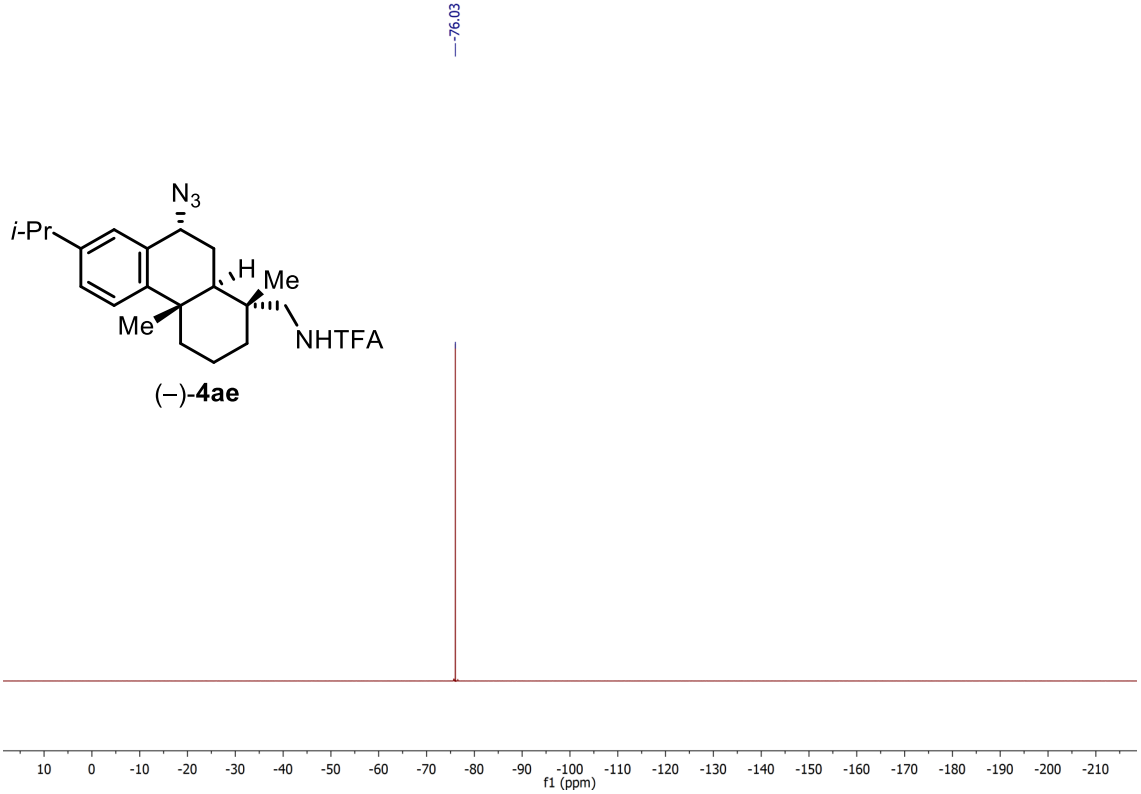
^{13}C NMR spectrum of a mixture of **3ad** and **4ad** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



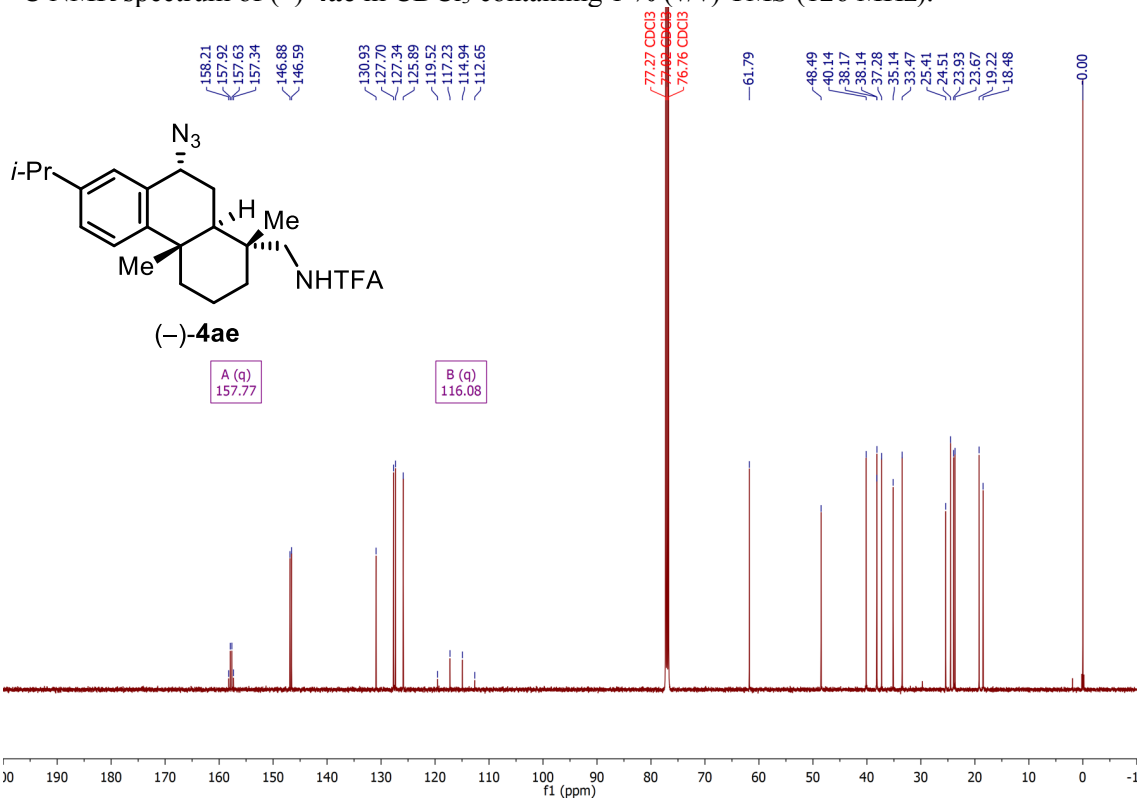
^{1}H NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



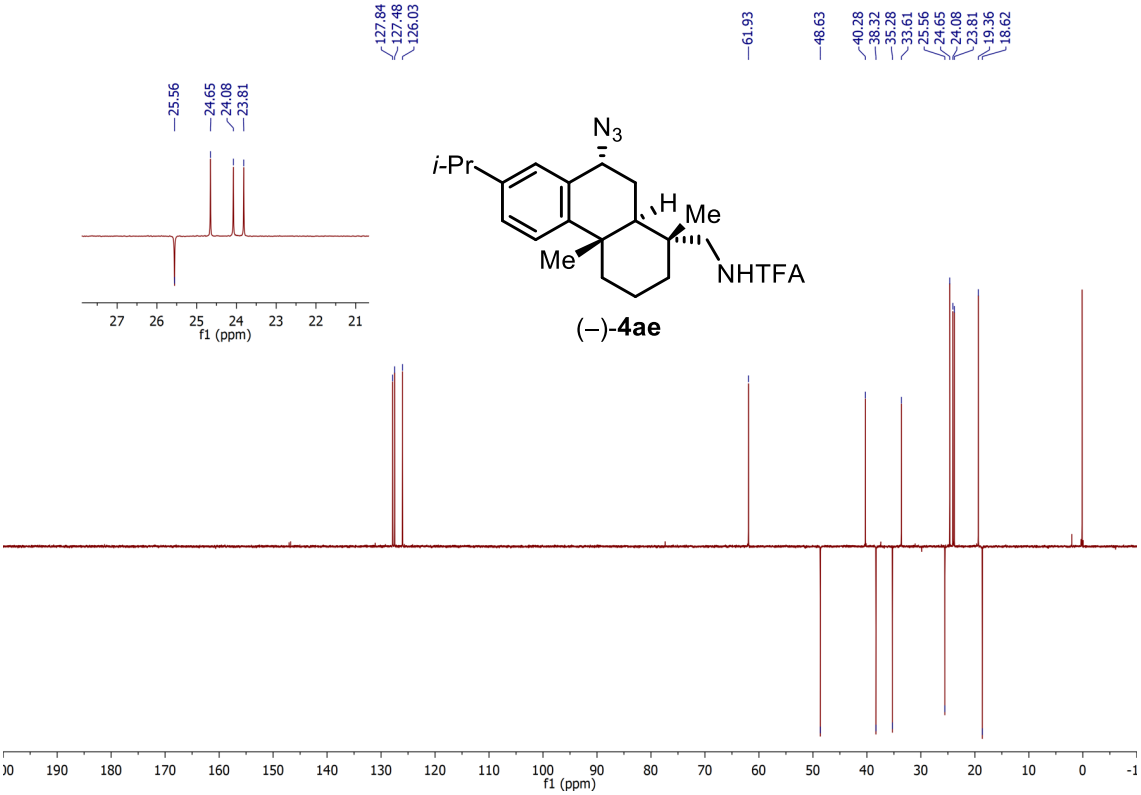
^{19}F NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



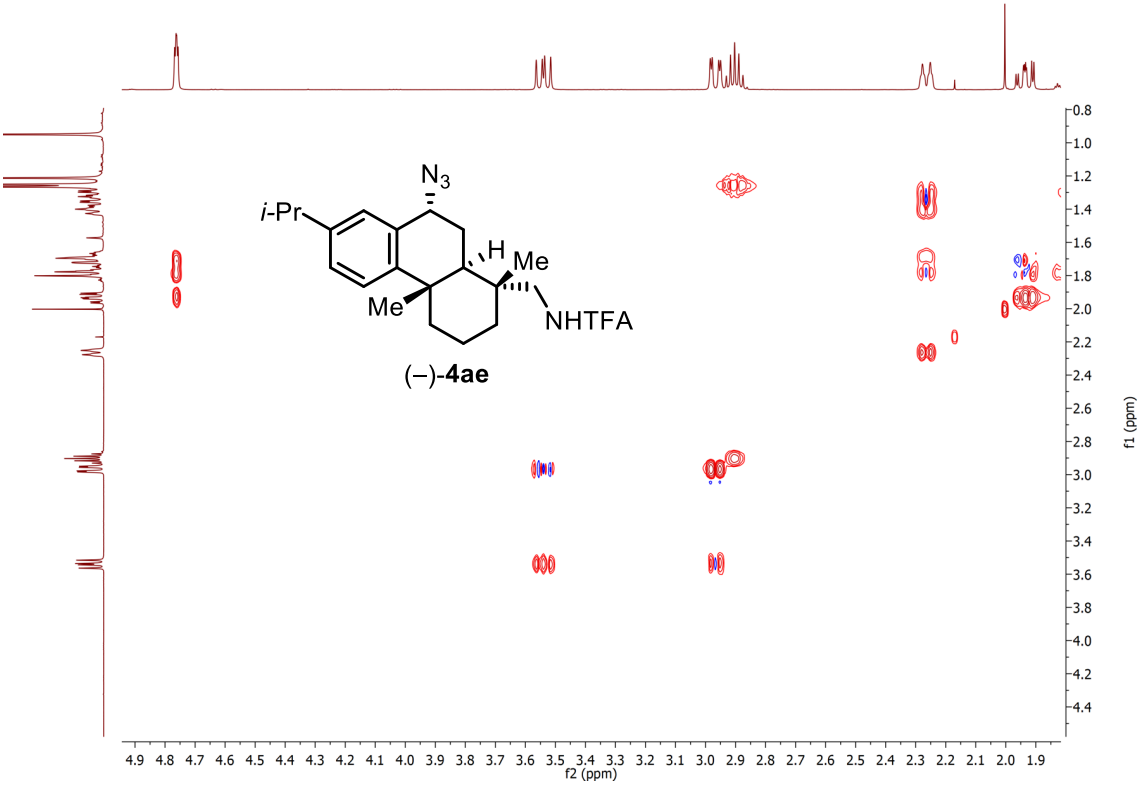
^{13}C NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



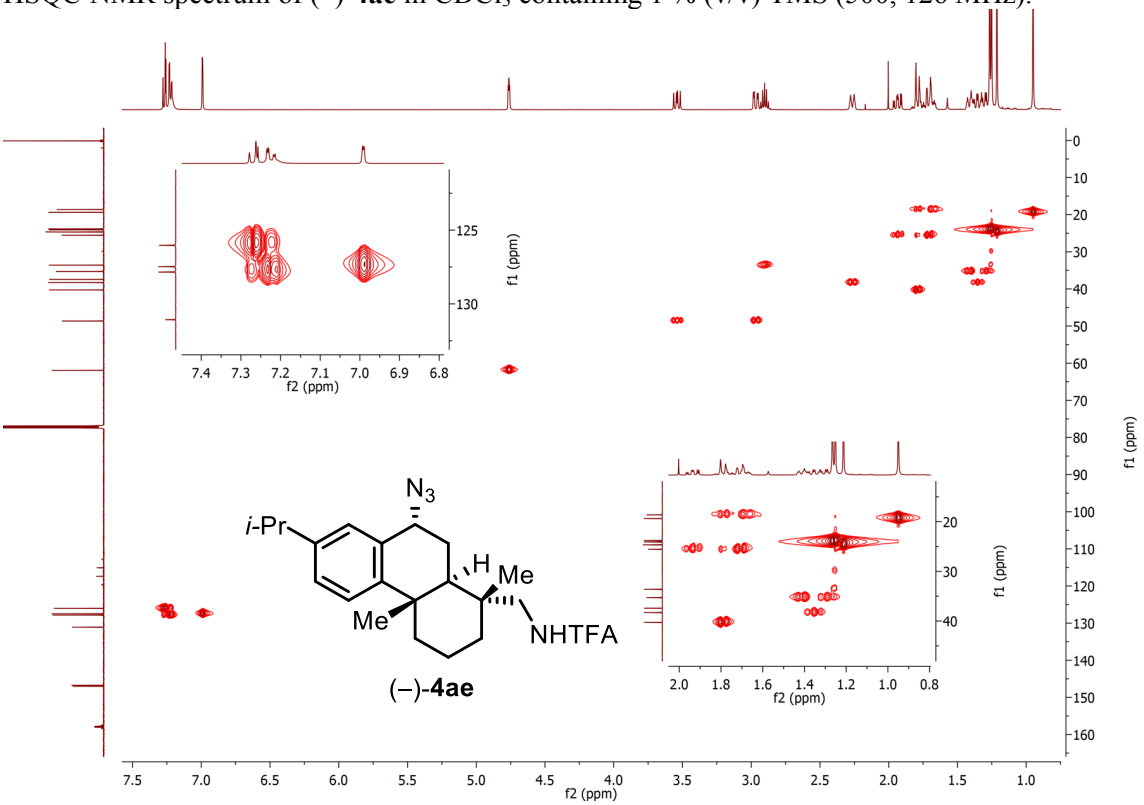
^{13}C DEPT-135 NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



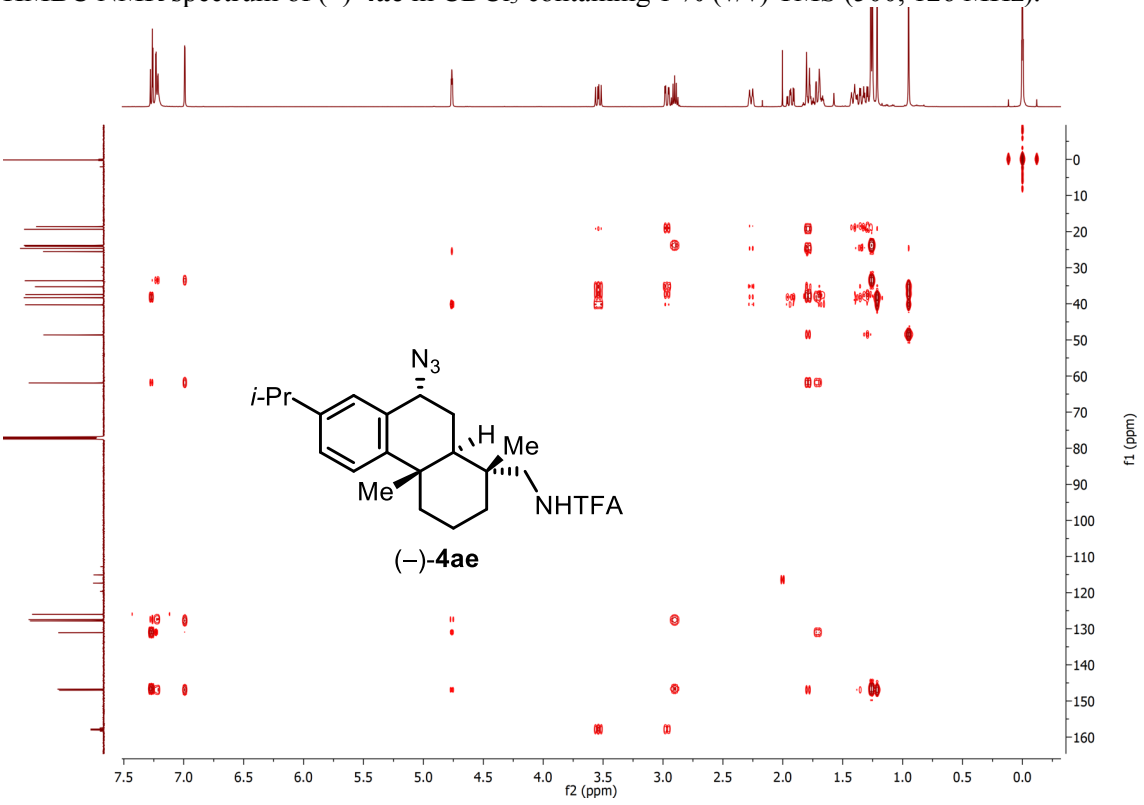
TOCSY NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (500, 500 MHz).



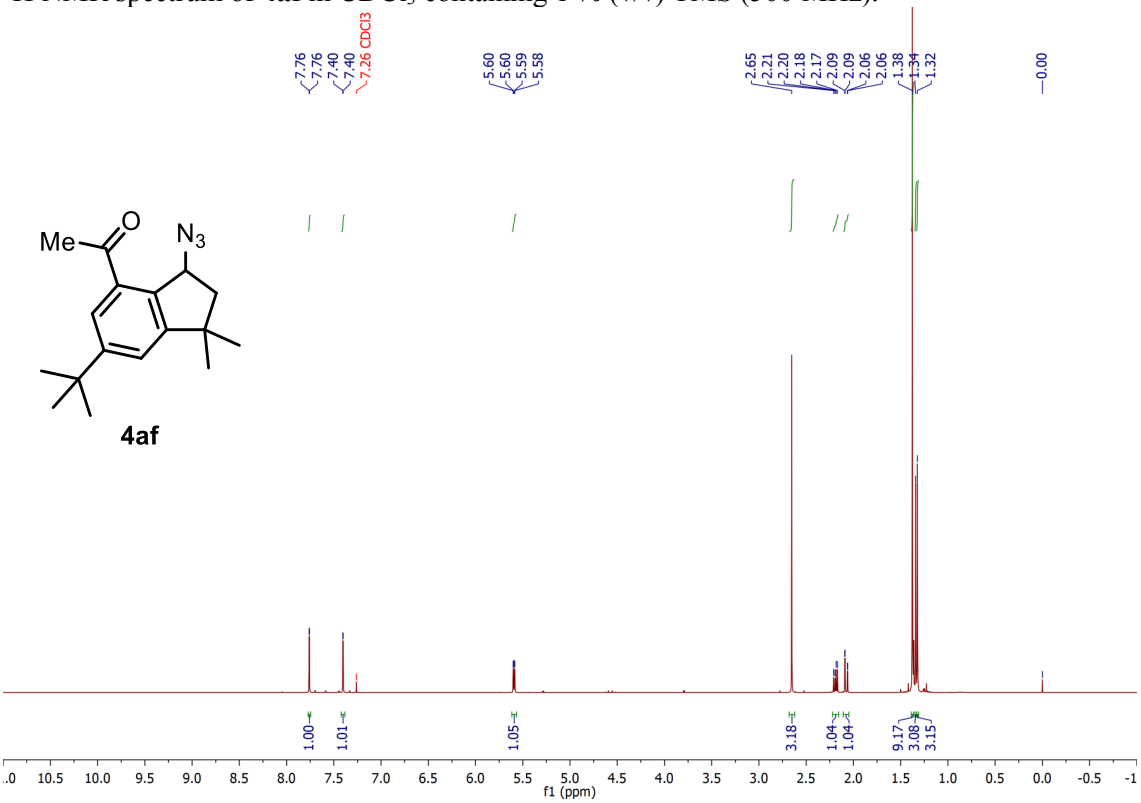
HSQC NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



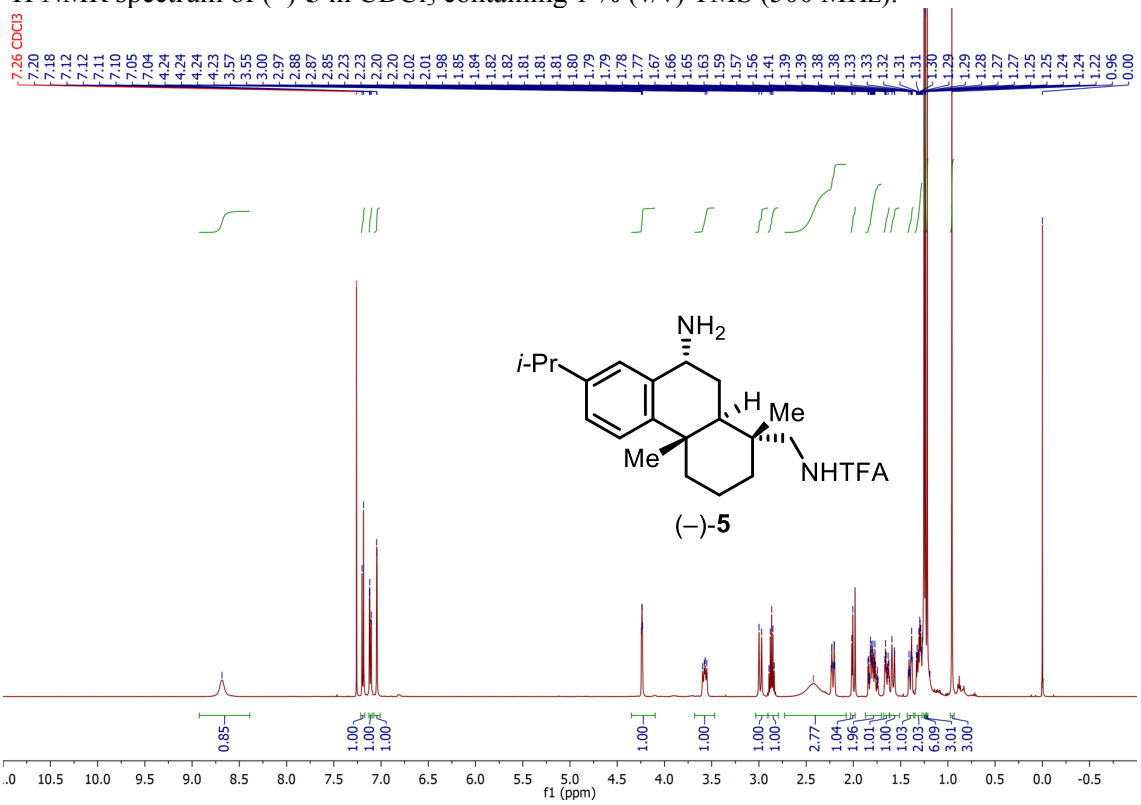
HMBC NMR spectrum of (–)-**4ae** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



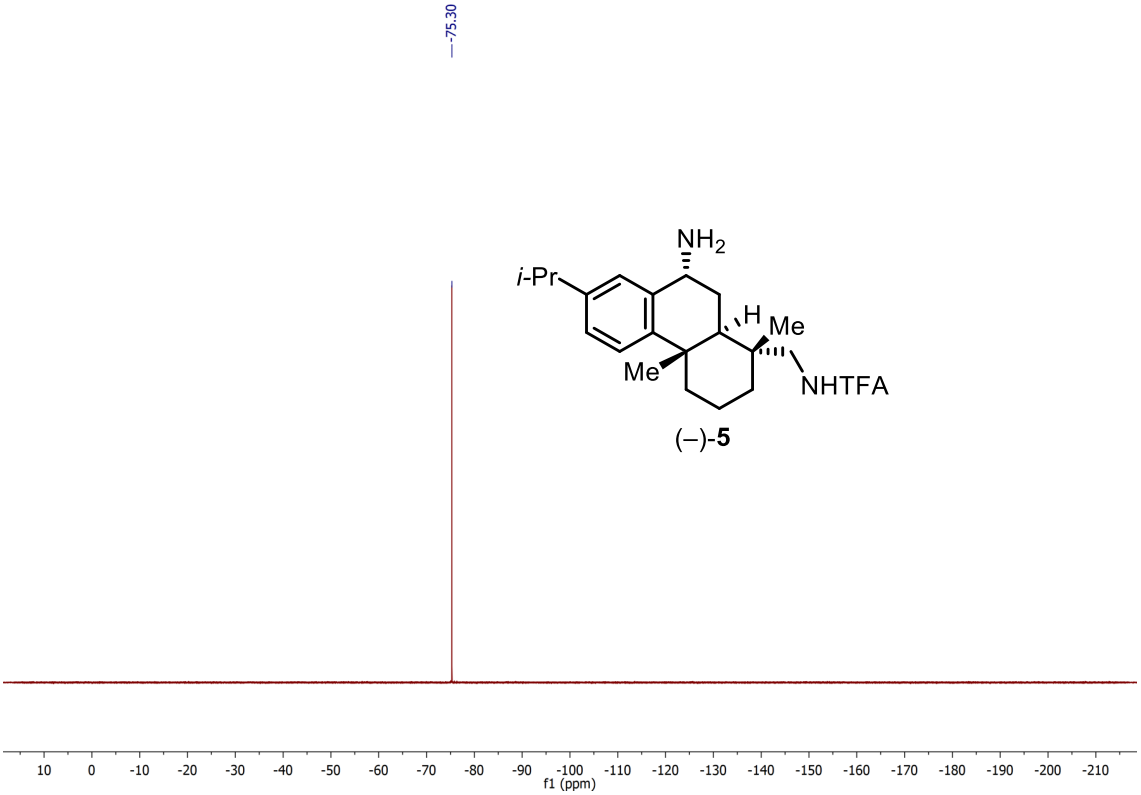
^{1}H NMR spectrum of **4af** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



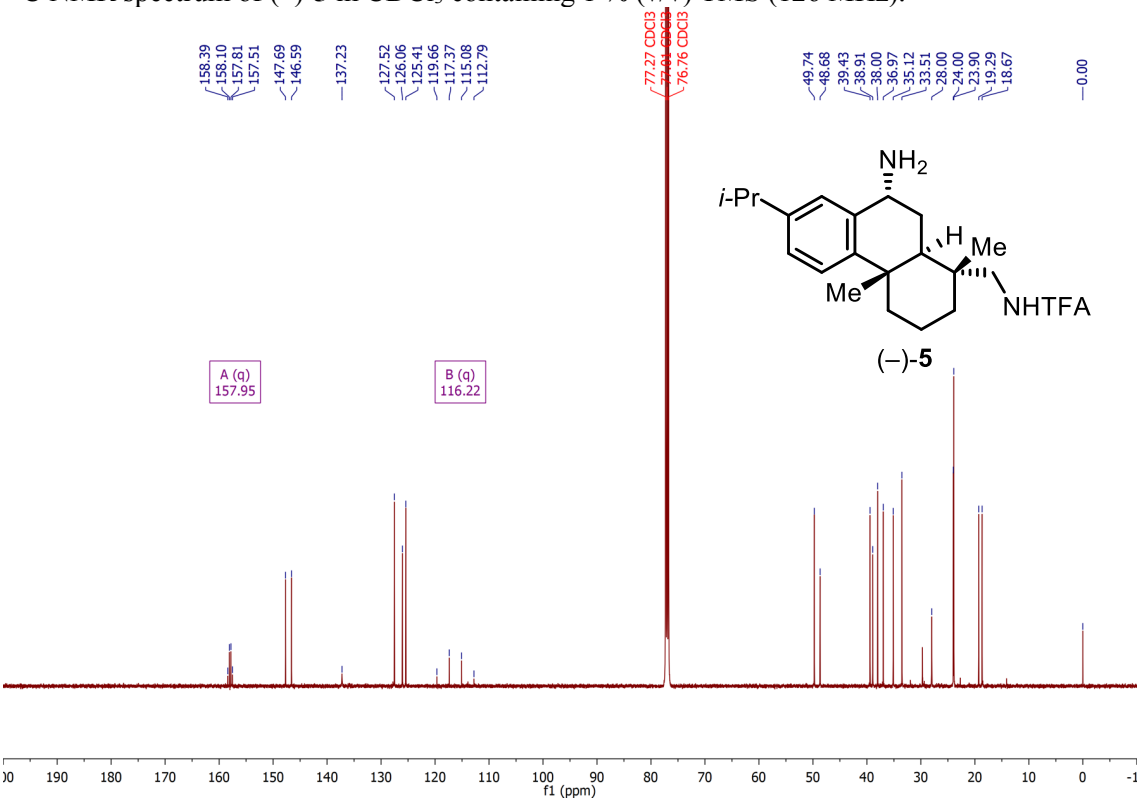
^{1}H NMR spectrum of (–)-**5** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



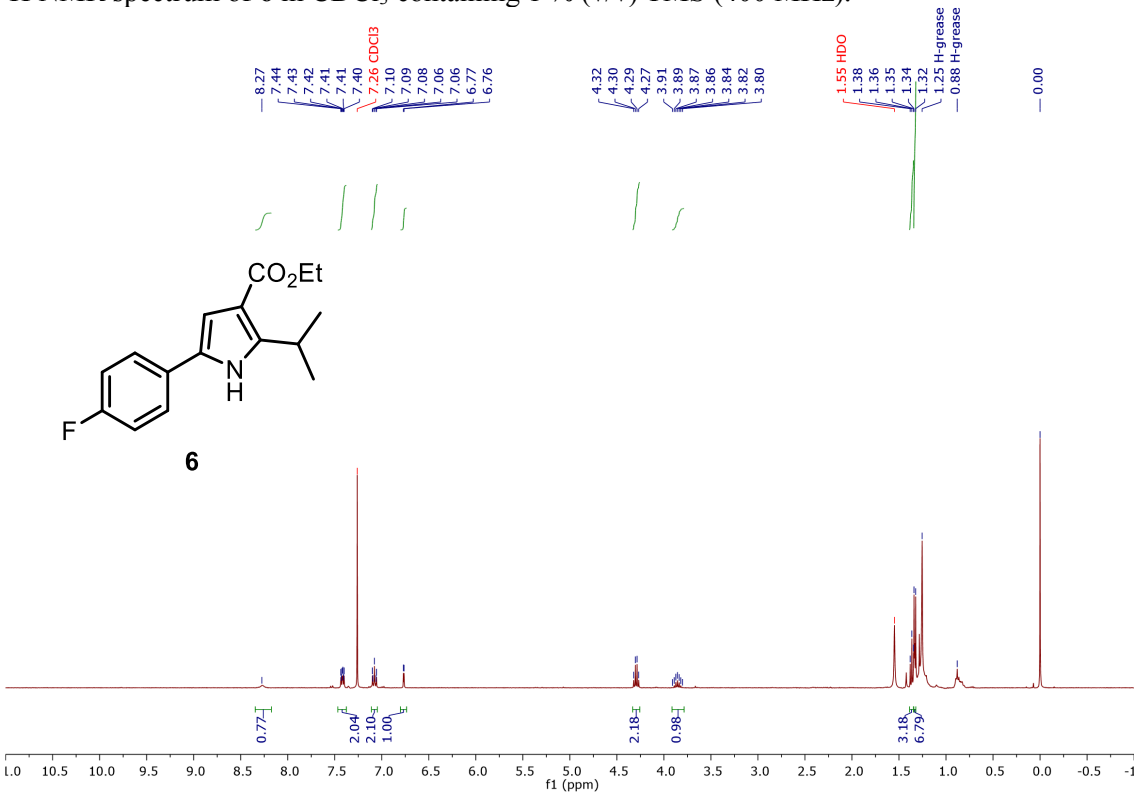
^{19}F NMR spectrum of (–)-**5** in $CDCl_3$ containing 1 % (v/v) TMS (377 MHz).



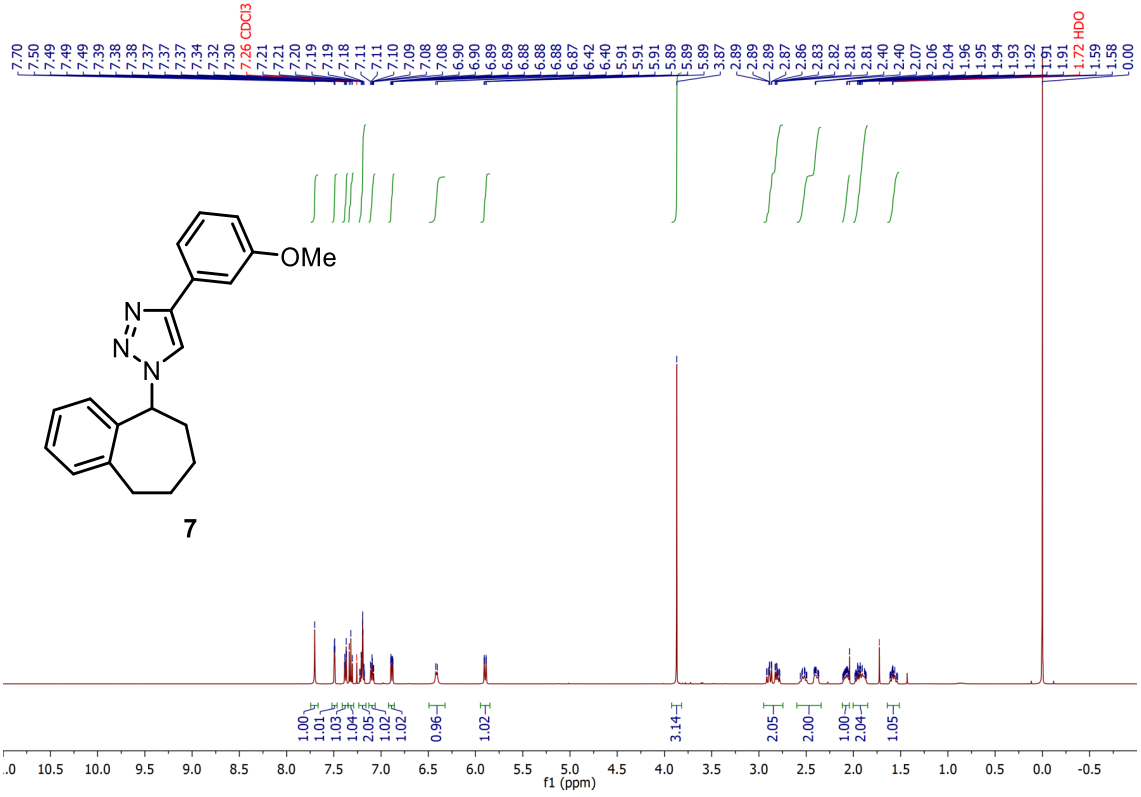
^{13}C NMR spectrum of (–)-**5** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



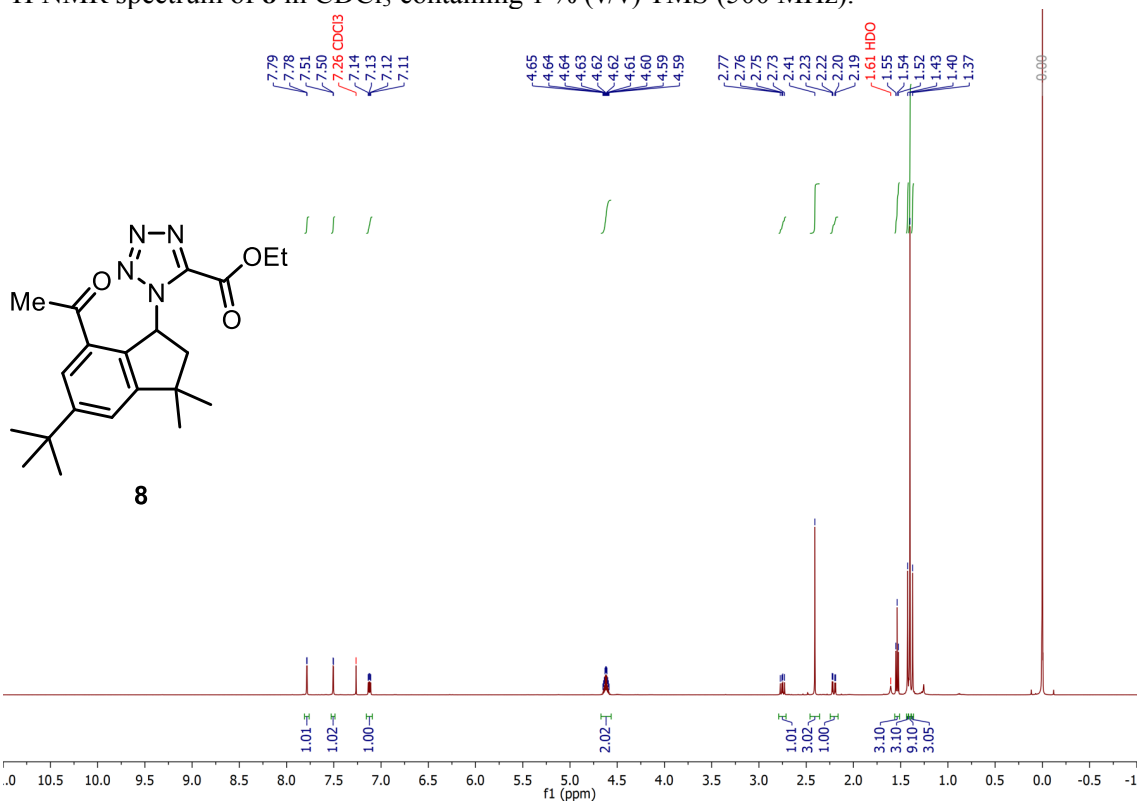
^{1}H NMR spectrum of **6** in $CDCl_3$ containing 1 % (v/v) TMS (400 MHz).



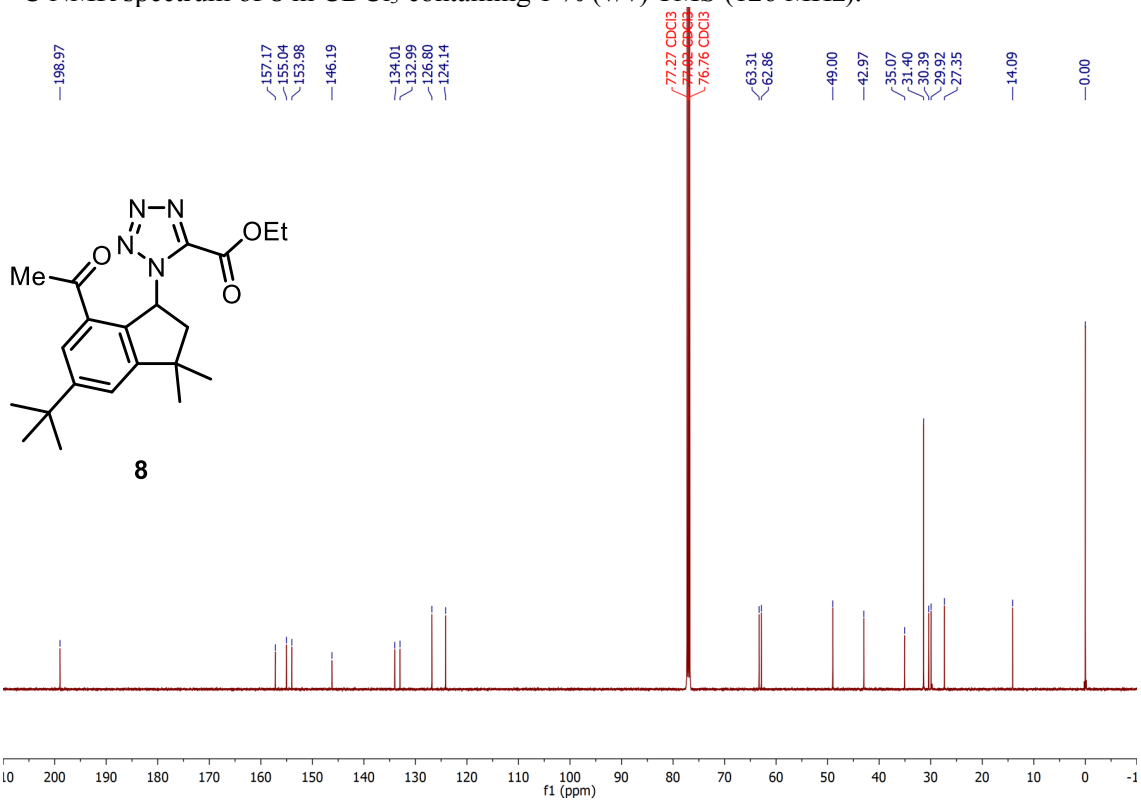
^{1}H NMR spectrum of **7** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



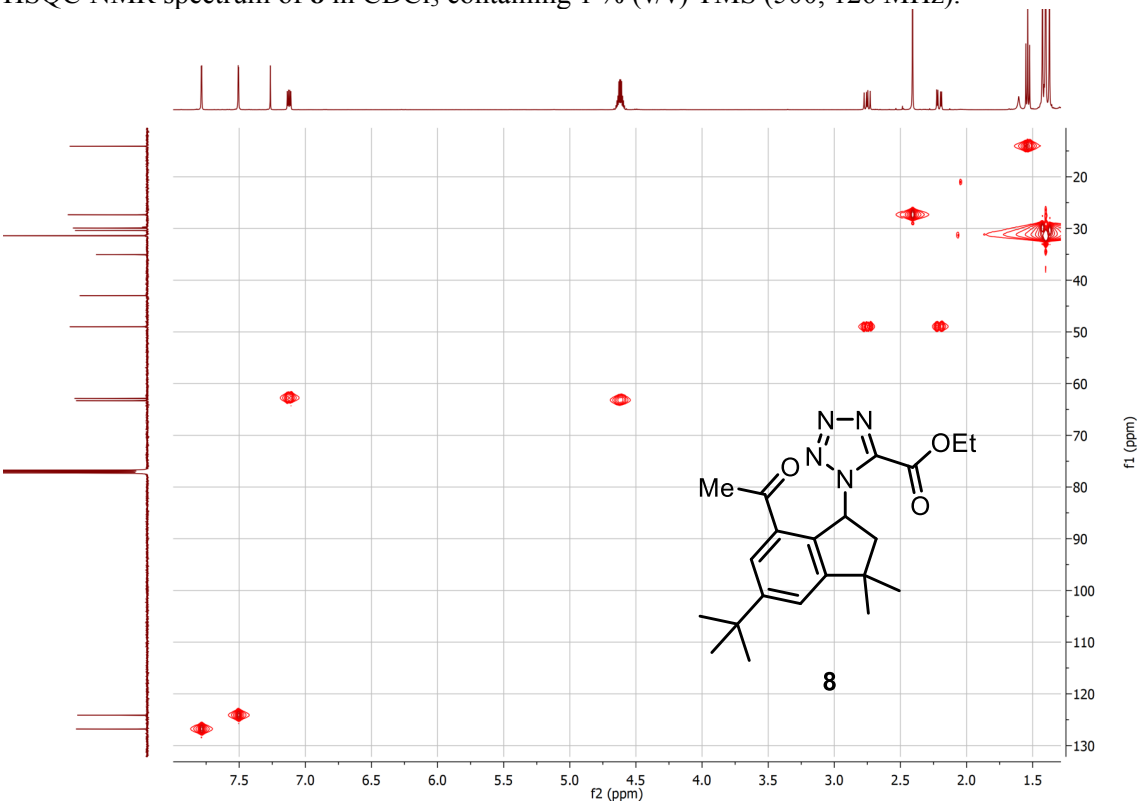
^{1}H NMR spectrum of **8** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



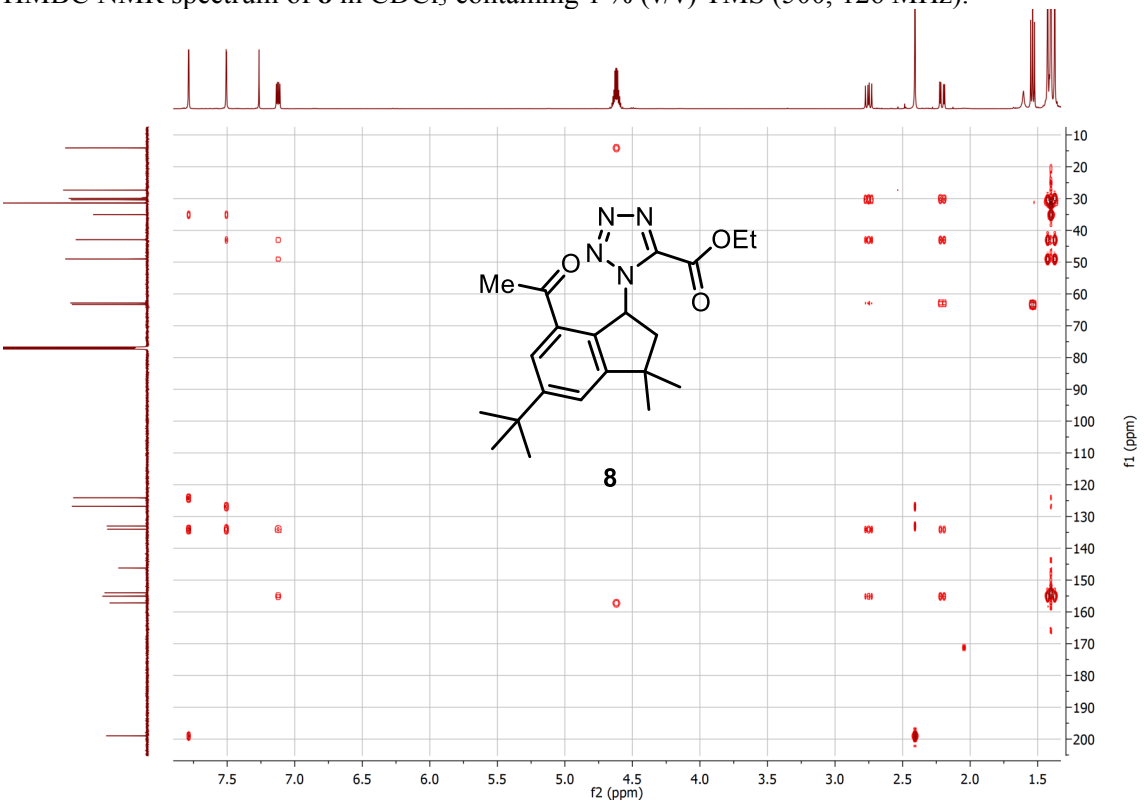
^{13}C NMR spectrum of **8** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



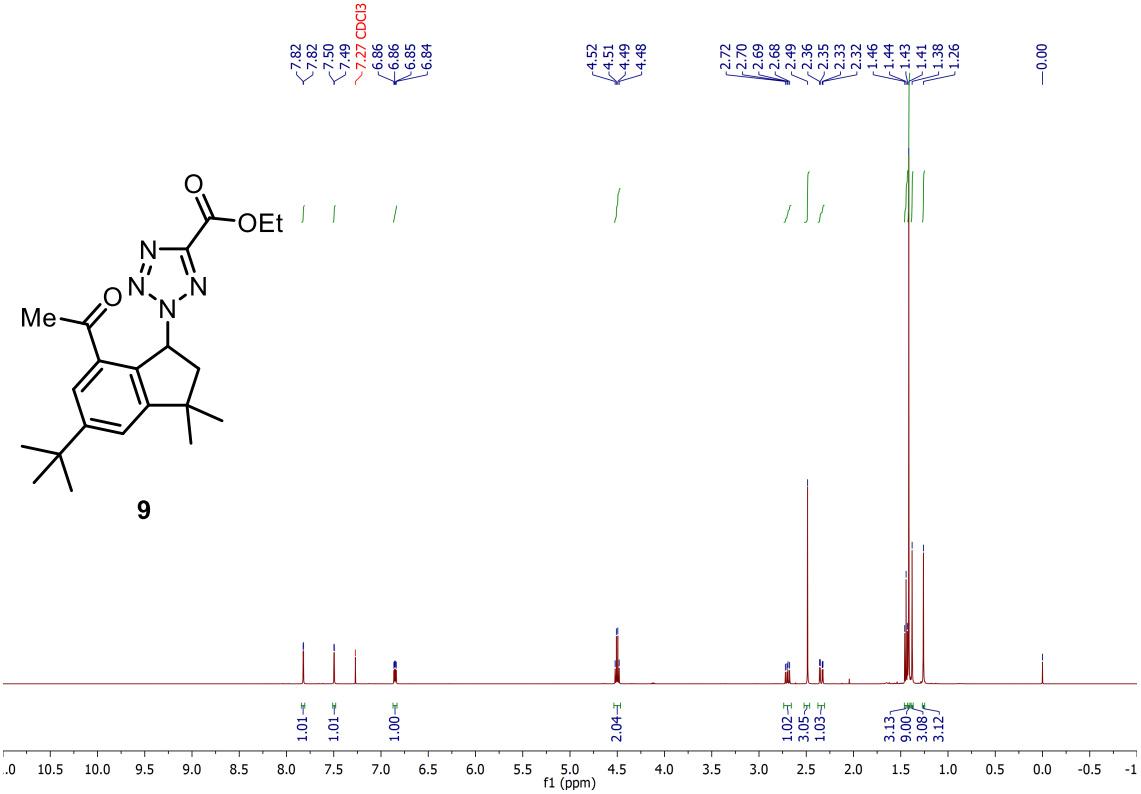
HSQC NMR spectrum of **8** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



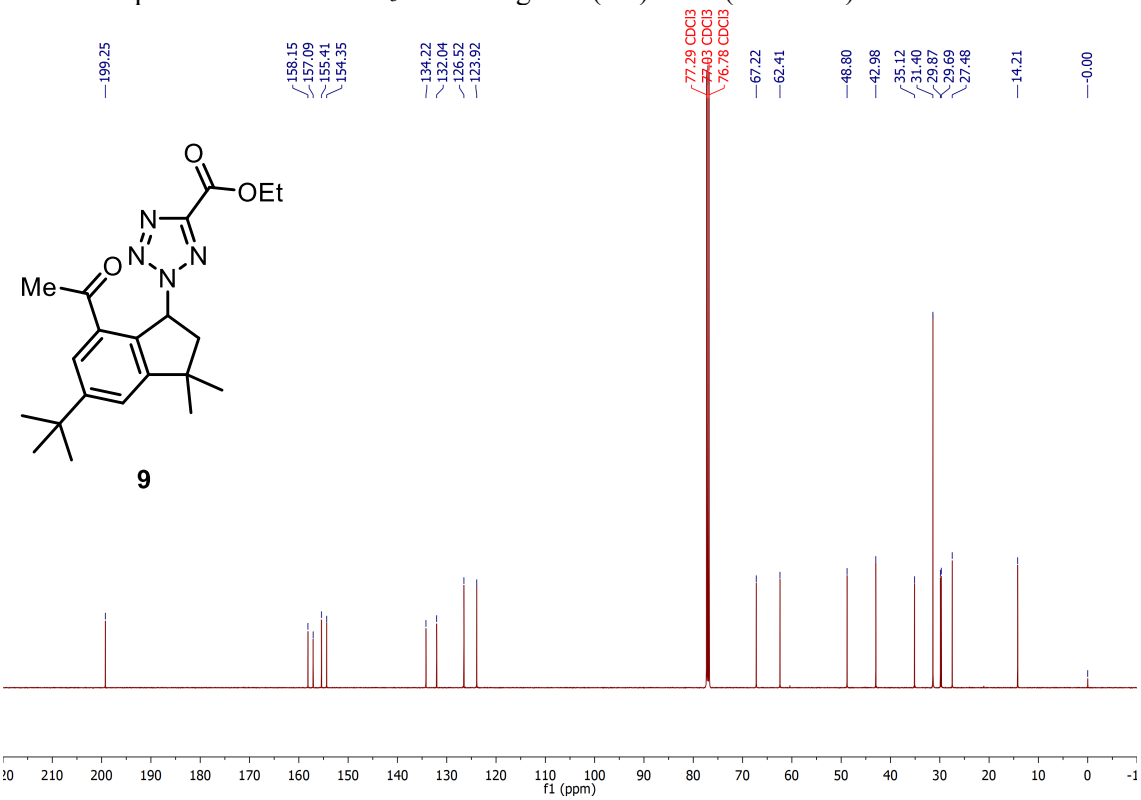
HMBC NMR spectrum of **8** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



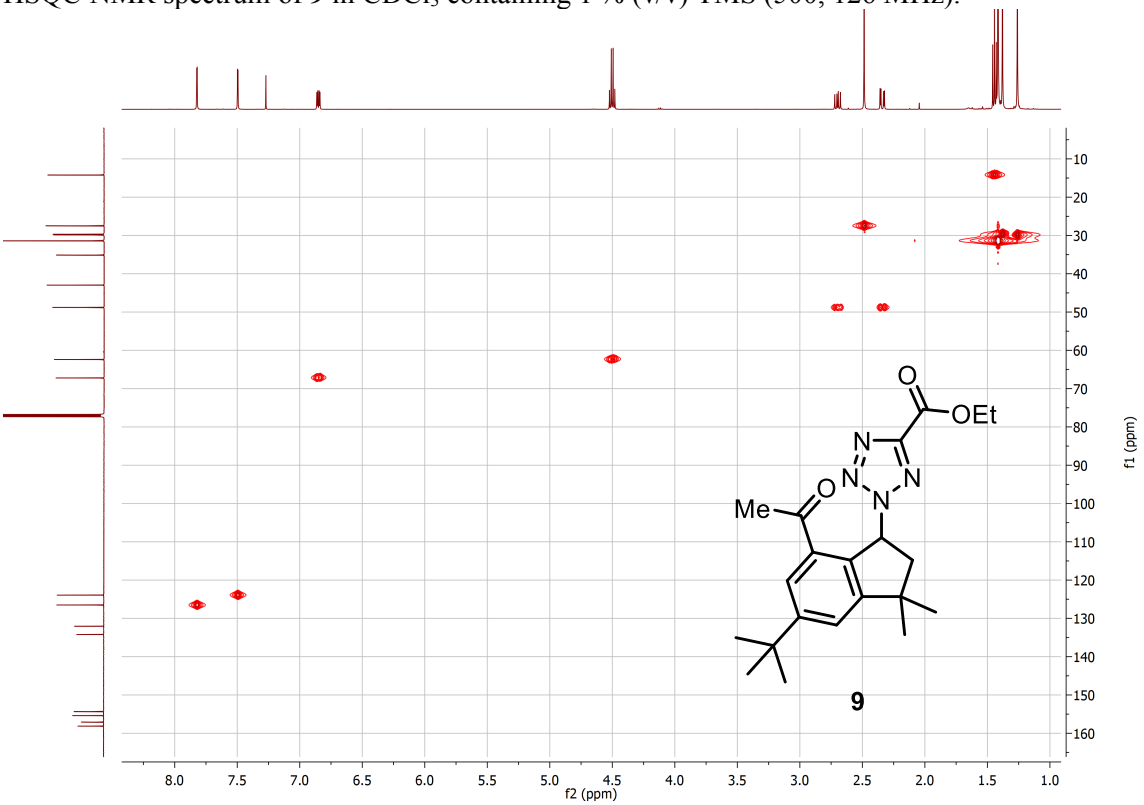
^{1}H NMR spectrum of **9** in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



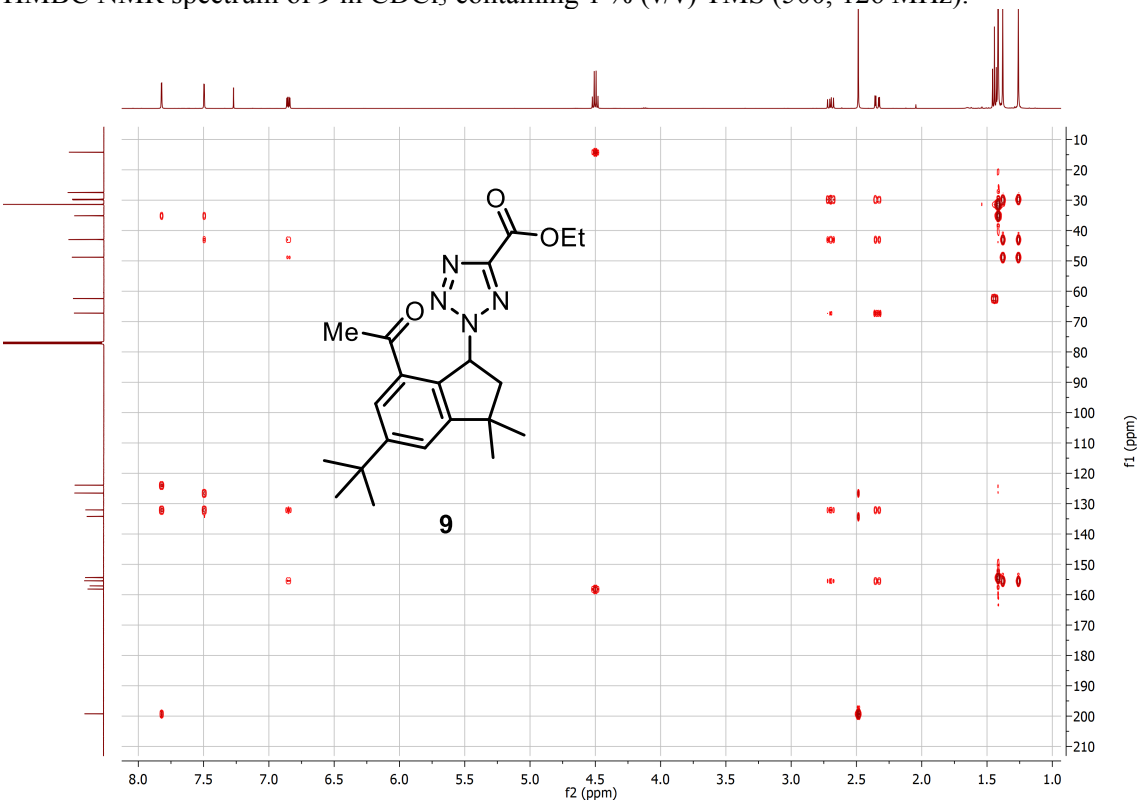
^{13}C NMR spectrum of **9** in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



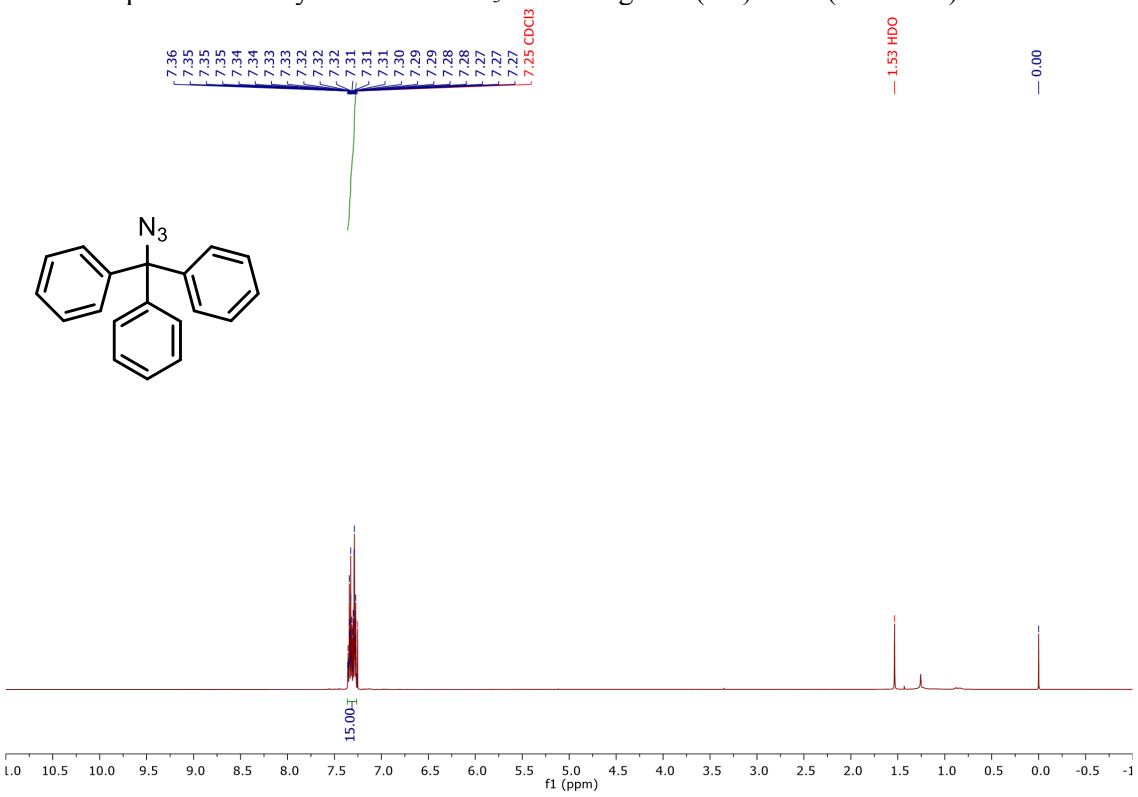
HSQC NMR spectrum of **9** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



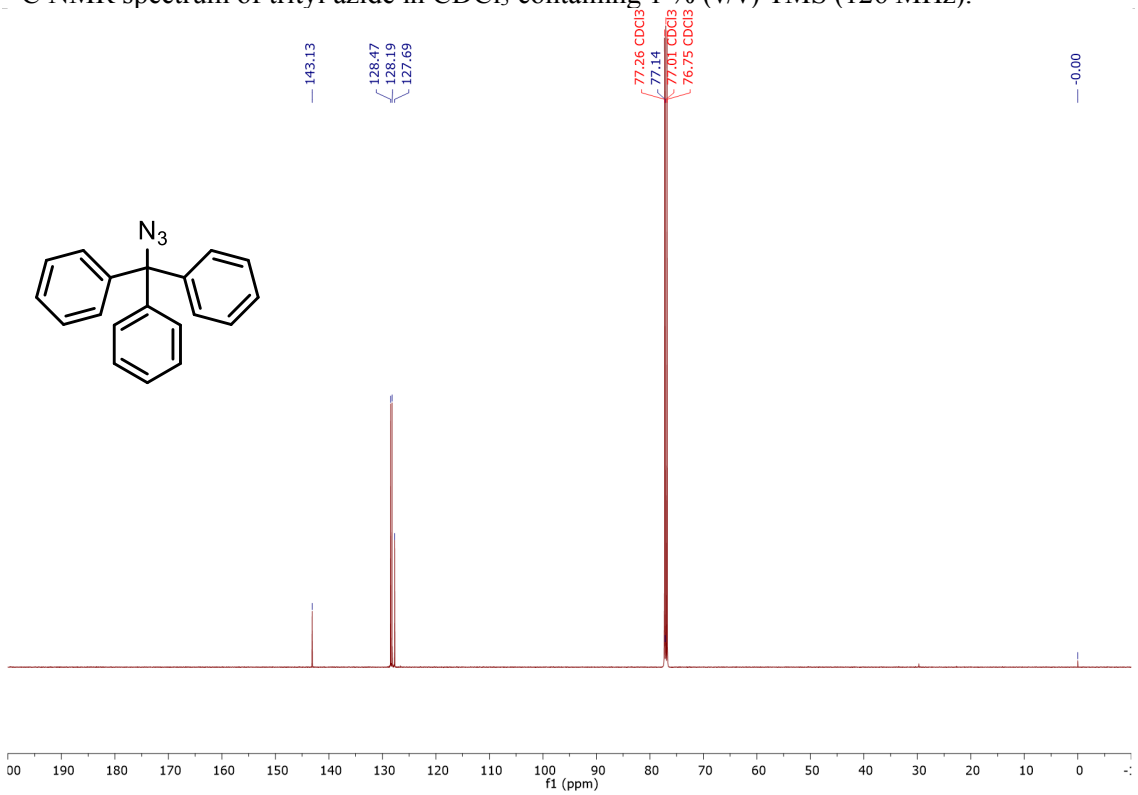
HMBC NMR spectrum of **9** in $CDCl_3$ containing 1 % (v/v) TMS (500, 126 MHz).



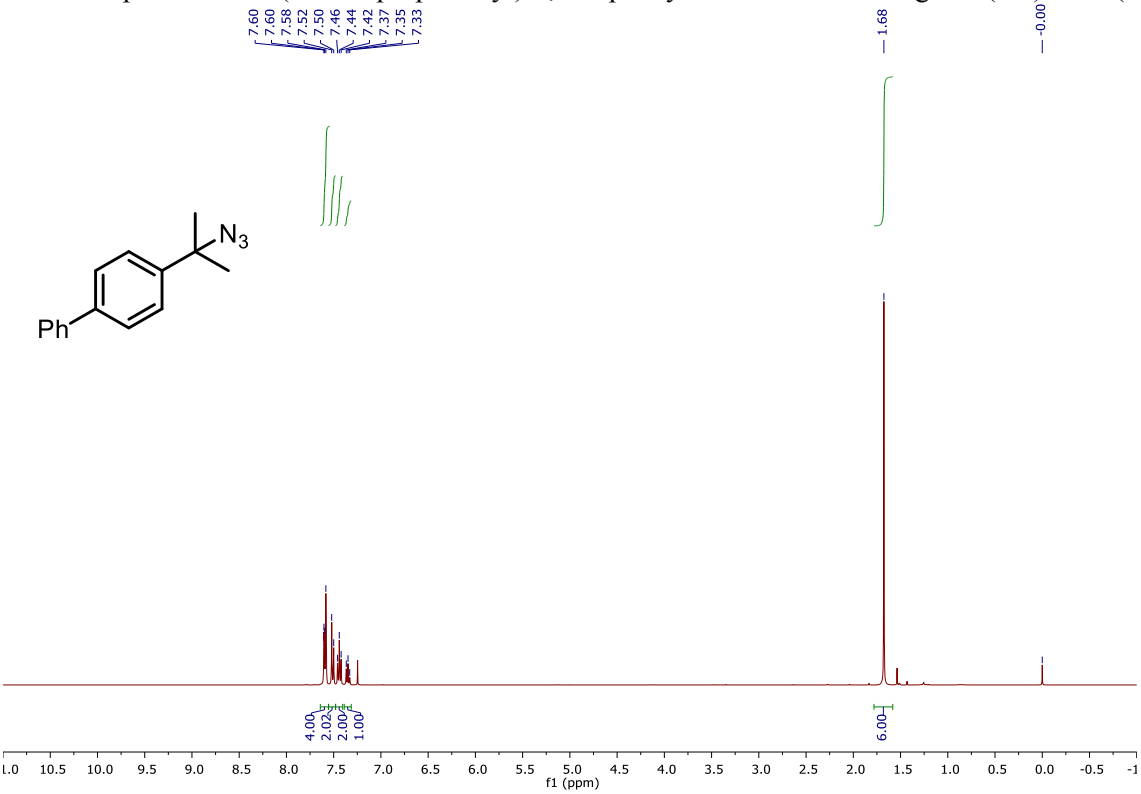
^{1}H NMR spectrum of trityl azide in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



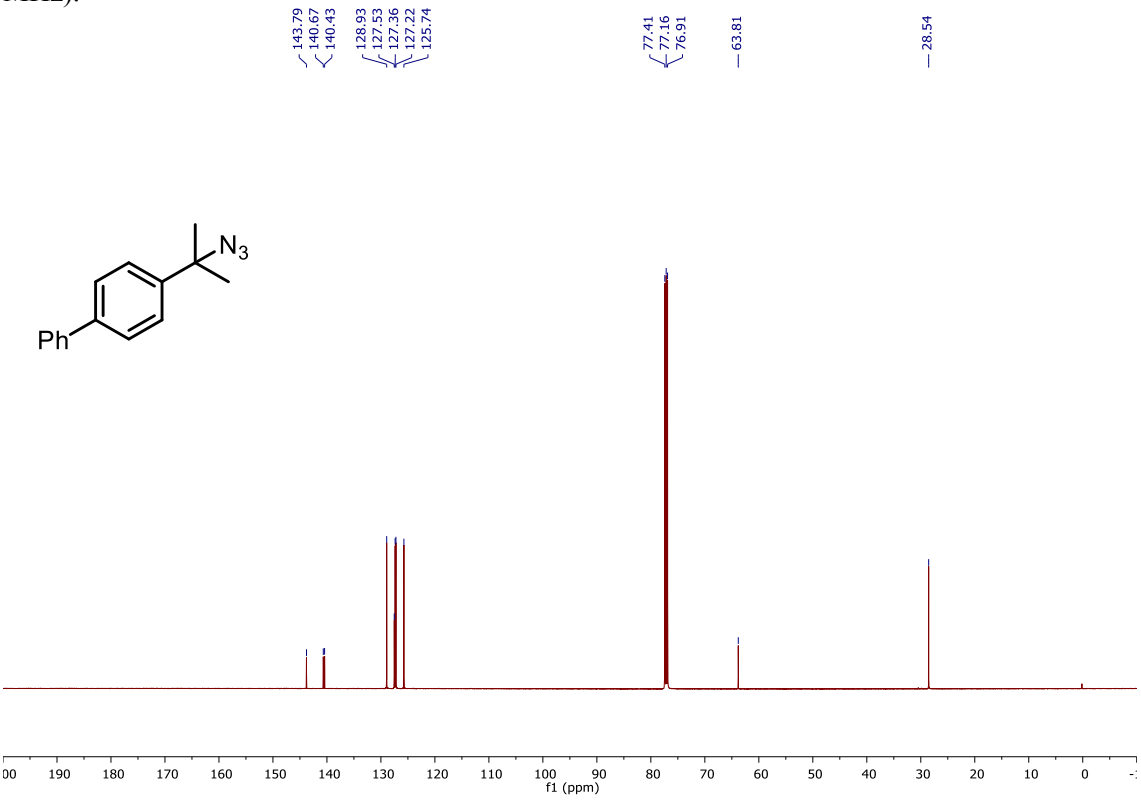
^{13}C NMR spectrum of trityl azide in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



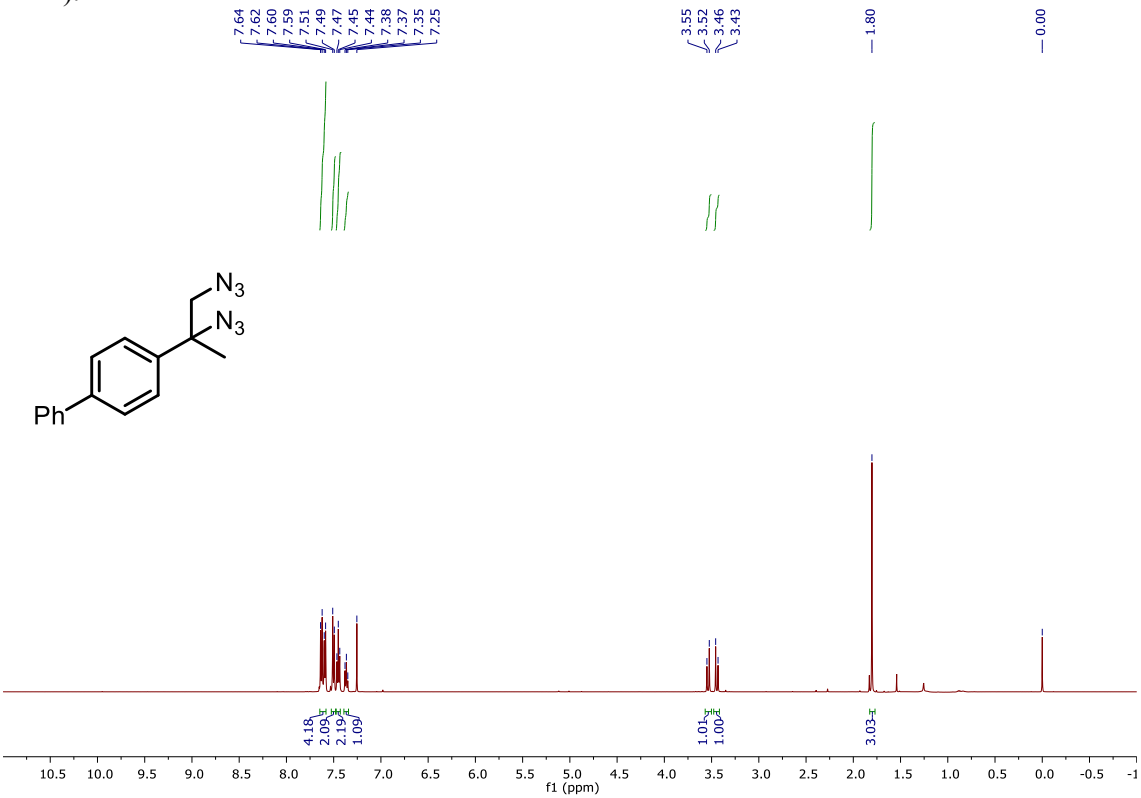
^{1}H NMR spectrum of 4-(2-azidopropan-2-yl)-1,1'-biphenyl in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



^{13}C NMR spectrum of 4-(2-azidopropan-2-yl)-1,1'-biphenyl in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).



^{1}H NMR spectrum of 4-(1,2-diazidopropan-2-yl)-1,1'-biphenyl in $CDCl_3$ containing 1 % (v/v) TMS (500 MHz).



^{13}C NMR spectrum of 4-(1,2-diazidopropan-2-yl)-1,1'-biphenyl in $CDCl_3$ containing 1 % (v/v) TMS (126 MHz).